

2011

Steam reforming of water-soluble fast pyrolysis bio-oil: Studies on bio-oil composition effect, carbon deposition, and catalyst modifications

Pedro J. Ortiz-toral
Iowa State University

Follow this and additional works at: <https://lib.dr.iastate.edu/etd>

 Part of the [Biological Engineering Commons](#), and the [Chemical Engineering Commons](#)

Recommended Citation

Ortiz-toral, Pedro J., "Steam reforming of water-soluble fast pyrolysis bio-oil: Studies on bio-oil composition effect, carbon deposition, and catalyst modifications" (2011). *Graduate Theses and Dissertations*. 11965.
<https://lib.dr.iastate.edu/etd/11965>

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

**Steam reforming of water-soluble fast pyrolysis bio-oil:
Studies on bio-oil composition effect, carbon deposition, and catalyst modifications**

by

Pedro J. Ortiz-Toral

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Brent H. Shanks, Co-major Professor
Robert C. Brown, Co-major Professor
R. Dennis Vigil
Robert Anex
D. Raj Raman

Iowa State University

Ames, Iowa

2011

Copyright © Pedro J. Ortiz-Toral, 2011. All rights reserved.

Table of Contents

List of Figures	iv
List of Tables	vi
Acknowledgements	vii
Chapter 1. General Introduction	1
Chapter 2. Recent Developments in Thermochemical Production of Hydrogen from Biomass	3
Abstract	3
Introduction	3
Biomass gasification	5
Pyrolysis of biomass	13
Biomass depolymerization by hydrolysis	20
Challenges	22
Conclusions	24
References	25
Chapter 3. Steam Reforming of Bio-oil Fractions: Effect of Composition and Stability	30
Abstract	30
Introduction	30
Experimental Section	33
Results and Discussion	40
Conclusions	51
References	53
Chapter 4. Steam Reforming of Bio-oil Model Compounds: Reactivity and Carbon Deposition Studies	56
Abstract	56
Introduction	57
Experimental	60
Results and discussion	62
Conclusions	71
References	72
Chapter 5. Steam Reforming of Acetic Acid over Mg and Co modified Ni/Al ₂ O ₃ catalyst	74
Abstract	74
Introduction	75
Experimental	79
Results and discussion	82
Conclusions	93
References	94

Chapter 6. General Conclusions	98
Appendix A. Initial Experimental Setups	102
Appendix B. Bio-oil and Catalyst Stability: Additional Observations	111
Appendix C. Evaluation of a Bimetallic NiCo at High Conversion	115
Appendix D. Combined Catalyst-Sorbent for Bio-oil Steam Reforming	121

List of Figures

Figure 1. Outline of strategies for thermochemical hydrogen production from biomass	5
Figure 2. General schematic of system for clean hydrogen generation	6
Figure 3. Schematic of gasifier coupled with syngas fermentation unit	12
Figure 4. Schematic diagram of the fast pyrolysis reactor with staged bio-oil collection unit used to produce bio-oil	32
Figure 5. Schematic diagram of the steam reforming system	37
Figure 6. Steady-state gas composition plots of catalytic and non-catalytic reactions	41
Figure 7. Hydrogen yield and carbon conversion to gas products for catalytic and non-catalytic reactions	41
Figure 8. Hydrogen yield for different water addition levels at T=500°C	43
Figure 9. Hydrogen yield based on amount fed of the different samples.	45
Figure 10. Carbon conversion to gas products and estimated fraction of carbon deposited from the different samples.	46
Figure 11. H ₂ stoichiometric yield of four of the samples reformed at T=500°C	47
Figure 12. Effect of concentration for the most relevant species in the bio-oil	49
Figure 13. Effect of storage time after water addition on hydrogen yield.	50
Figure 14. Effect of filtration of aged bio-oil solution	51
Figure 15 Tests for transport limitations with acetic acid as probe molecule	63
Figure 16 Overall conversions of model species during steam reforming reactions	64
Figure 17. TPO profile from SR of acetic acid at 420°C	65
Figure 18 Catalytic steam reforming, carbon deposition	66
Figure 19. Non-catalytic steam reforming, carbon deposition	67
Figure 20. Catalytic coking comparison for acetic acid and acetone	69
Figure 21. Carboxylic acid coke deposition study	70

Figure 22. Steam-TPO of carbon deposits after acetic acid SR at 460°C	83
Figure 23. XRD analysis of the reduced Ni catalysts over pure and mixed Al and Mg supports	85
Figure 24. Coke as function of hydrogen generation at 460°C	86
Figure 25. Coke as function of hydrogen generation at 650°C	87
Figure 26. XRD analysis of the reduced Ni-Co catalysts compared to Ni/Al	90
Figure 27. Coke as function of hydrogen generation for NiCo catalysts at 460°C	91
Figure 28. Coke as function of hydrogen generation for NiCo catalysts at 650°C	92

List of Tables

Table 1. Gas Composition at Various Locations in the Gas Conditioning System	11
Table 2. Characterization of the four whole bio-oil fractions.....	34
Table 3. Composition of the different aqueous bio-oil extracts.....	43
Table 4. Elemental analysis of the set of aqueous samples	48
Table 5. Model compounds and stoichiometry of steam reforming to H ₂ and CO ₂	59
Table 6. Mg modified catalyst characterization.....	84
Table 7. SR reaction testing results for Mg modification tests.....	85
Table 8. Co modified catalyst characterization.....	89
Table 9. SR reaction testing results for Co modification tests.....	90

Acknowledgements

I would like to acknowledge the patient guidance of my supervisors Brent H. Shanks and Robert C. Brown throughout the course of this doctorate degree. Their careful direction and consistent challenge was key in the completion of this work. Thanks also for their tips in professional development and skills that have made my learning experience much more wholesome.

I would like to also give credit to my colleagues from Brent H. Shanks' and CSET research groups and staff for their support and our engaging technical discussions. My sincere thanks to the undergraduate assistants who were in one way or another part of this project, especially to Martin K. Dufficy, Steve Nye (REU program), Nataly Aleman, and Evan Moser.

Thanks to my fellow colleagues from the NSF-AGEP (Alliance for Graduate Education and the Professoriate) and GMAP (Graduate Minority Assistantship Program), also the extremely talented staff and all individuals associated with these programs with whom I constructively interacted.

A very special thanks to my wife Liznel to whom I dedicate this dissertation. Her loving support, patience, and understanding truly made this work possible. Thanks to my parents, sisters, and extended family for their loving support and words of encouragement. Thanks to the people in the Ames community that have become like family to me and my wife. Special thanks to John McCully and Ruth, and Jim Merideth and Mercedes.

I would also like to acknowledge the financial support from the United States Department of Agriculture, the NSF-AGEP program, and the ISU Bioeconomy Institute.

Above all thanks to God through whom all things are possible.

Chapter 1. General Introduction

Bio-oil or its heavy fractions can be catalytically upgraded to liquid fuels that are compatible with the current transportation infrastructure. These bio-oils from fast pyrolysis of lignocellulosic biomass can be phase separated into a heavy water insoluble portion and a light water-soluble portion. The heavy bio-oil portion has been deemed more suitable for upgrading since it tends to contain molecules that are less oxygenated and are more compatible with the present crude oil refining technologies than the water-rich portion. The water-rich portion contains mainly carboxylic acids, carbohydrates, aldehydes, ketones and alcohols. This highly oxygenated water-rich portion is better suited for production of the renewable hydrogen required for the upgrading reactions. There are certain challenges introduced due to the complexity of these mixtures. Catalyst deactivation by coking and the formation of carbon deposits are major limitations although the specific causes were previously unidentified. It was proposed that these limitations could be reduced by selectively reforming specific fractions of the bio-oil. A bio-oil fractionating system can separate heavier components from the light-end components. This light-end fraction has shown to be better suited for hydrogen production via steam reforming at moderate temperatures generating mainly hydrogen and carbon dioxide. Due to their chemical instability the bio-oils showed evident aging leading to decreased hydrogen production potential when stored for long periods of time. Also it must be noted that the ash content from biomass that ends up in the bio-oil tends to accumulate on the catalyst over time leading to decrease in activity.

Model compounds representing the water-soluble components we compared in controlled tests to find troublesome species in terms of resistance to reaction and carbon deposition tendency. Experiments were performed under kinetic control conditions at low conversions to reveal reaction characteristics while avoiding thermodynamics and transport limitations. It was found that levoglucosan, acetic acid, and furfural were the species with the highest limitation in terms of carbon deposition leading to decreased hydrogen production and low catalyst stability. Levoglucosan was found to decompose more easily leading to carbon deposition even in the absence of a catalyst. Acetic acid and furfural were then found to tend

to coke over the catalyst but where mostly thermally stable. With the potential of efficiently separating the carbohydrate components and the furan derivatives from the light-end fraction we face with acetic acid being the main troublesome compound. Focusing on acetic acid as a model compound in a systematic manner can lead to an improved understanding of the routes of coke deposition to be able to ultimately minimize coking. With this purpose a catalyst modification was proposed to test the possibility of hindering coke formation at low temperature ranges as well as improved gasification properties to remove the deposits. These results will provide insight on the role of the metal and the support on the formation and removal of coke deposits and how the catalysts could be modified to improve the selectivity towards hydrogen production.

Dissertation organization

This dissertation is organized in chapters mainly corresponding to manuscripts to be published in important scientific journals. Chapter 2 provides a general background introducing the thermochemical production of hydrogen from biomass. Chapters 3 and 4 cover the first two stages of original research on the effect of chemical composition on steam reforming products and carbon deposition based on fractionated bio-oil and model species respectively. Chapter 5 lays out the study of reforming catalyst modification to reduce coke deposition from acetic acid as a troublesome bio-oil model compound. General conclusions are presented as Chapter 6 including some recommendations for future research. A set of appendices are included with supporting data and additional material.

Chapter 2. Recent Developments in Thermochemical Production of Hydrogen from Biomass

Pedro J. Ortiz-Toral^{1,2}, Robert C. Brown^{2,3}

Abstract

Hydrogen can be generated from biomass by a number of processes. These include biomass gasification coupled with gas-cleanup and water-gas shift, bio-oil reforming, bio-oil gasification, and aqueous-phase processing of biomass. None is clearly superior to the others with the choice depending upon such factors as the nature of the feedstock, reaction limitations and the size of the processing plant. Recent progress in production of hydrogen from biomass is discussed including challenges associated with each process.

Introduction

Hydrogen has many application ranging hydrogenating vegetable oils in the food industry to refining petroleum in transportation fuels and commodity chemicals. It is generated primarily from the steam reforming of natural gas. Although hydrogen will continue to be used in these applications, it will find increasing application in deoxygenating biomass-derived molecules into hydrocarbons suitable for fuels and commodity chemicals.[1-3] Although natural gas supplies are likely to remain secure in many parts of the world, its conversion to hydrogen contributes significantly to green house gas emissions into the atmosphere and the industry is under pressure to identify renewable sources of hydrogen. Although electrolysis of water using electricity from solar photovoltaics or wind power is often touted as future sources of hydrogen, in fact, thermochemical production of hydrogen from biomass is currently the most cost-effective source of renewable hydrogen at present and is likely to remain the leader for many years.

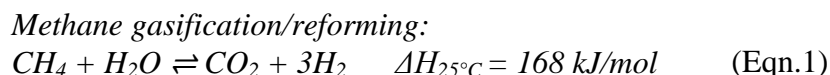
¹Department of Chemical and Biological Engineering,

²Center for Sustainable Environmental Technologies,

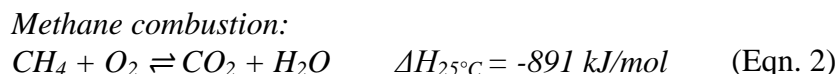
³Department of Mechanical Engineering; Iowa State University, Ames IA 50011, USA

About 59% of worldwide hydrogen production comes from catalytic steam-methane reforming (SMR) of natural gas. The use of natural gas for this purpose generates roughly 30 million tones per year of carbon dioxide (CO₂).[4,5] Production of hydrogen from biomass would greatly reduce net CO₂ release since the carbon is annually cycled between the atmosphere and growing biomass through photosynthetic fixation.[6-8] Although natural gas remains a relatively inexpensive source of hydrogen at present, there is increasing interest in replacing it with renewable sources of hydrogen to reduce net greenhouse gas emissions.[9]

It is important to recognize that most “sources of hydrogen” are actually sources of both hydrogen and energy to chemically extract hydrogen from water. For example, natural gas contains 2 moles of H₂ but upon gasification with steam yields up to 3 moles of hydrogen:



The thermal energy for this endothermic reaction comes from burning natural gas in air:



Accounting for the overall methane consumption, the net yield of hydrogen is 2.52 moles per mole of methane when combustion of 1 mol of methane provides heat for gasifying other 5.3 moles. Other so-called sources of hydrogen, such as coal and biomass, contain relatively lesser amounts of hydrogen and depend even more heavily upon the reaction of carbon with steam to yield hydrogen.

As shown in Figure 1, there are three primary thermochemical pathways for production of hydrogen from biomass: gasification, pyrolysis, and hydrolysis. Thermochemical processing of biomass is conducted over a wide temperature range, depending upon the process. Gasification occurs at temperatures above 800°C, pyrolysis occurs around 500°C, and hydrolysis is performed below 100°C. The products of gasification, pyrolysis, and hydrolysis are intermediates rather than hydrogen: syngas, bio-oil, and sugars, respectively. These products must be further treated to obtain hydrogen, as described below.

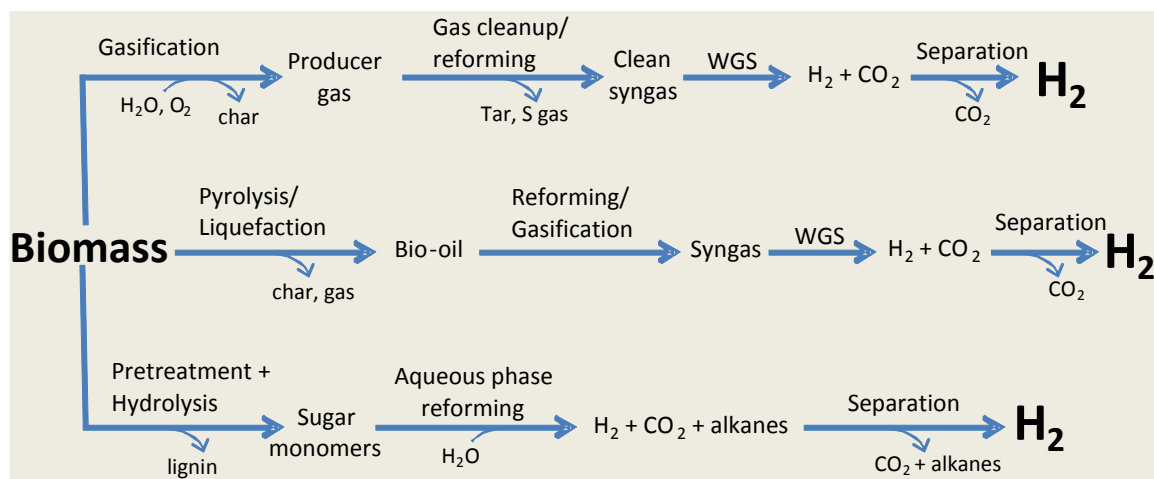


Figure 1. Outline of recently highlighted strategies for thermochemical hydrogen production from biomass

Biomass gasification

Gasification is a combination of mostly endothermic reactions that decompose and volatilize biomass feedstock (pyrolysis) and exothermic oxidation reactions (combustion) that provide the energy to sustain pyrolysis. These reactions occur in the temperature range of 600–1200 °C, with solid biomass decomposing to gaseous products including H_2 , CO, CO_2 , CH_4 and water along with some ash, char, tars, as well as amounts of H_2S . [10] Gasification systems are often classified according to the method by which energy is supplied to the gasifier: air blown, oxygen blown and indirectly heated. Air blown gasification is the simplest way to provide oxygen for combustion reactions while oxygen-blow gasification requires air-separation equipment to provide pure oxygen for combustion with the advantage that little molecular nitrogen dilutes the product gas, as it does for air-blown gasification. Indirectly heated gasification does not provide oxygen to the reactor at all, instead providing energy to the reactor by various heat transfer schemes. In fact, indirectly heated gasification is something of a misnomer as the process is really pure pyrolysis in the absence of combustion. Gasifiers can further be classified according to the gas-solid contact mechanism employed in the reaction vessel: moving beds (updraft or downdraft), fluidized beds or entrained flow reactors, descriptions of which can be found in the literature. [11-14]

The gas mixture composition will depend on biomass type, reactor type and process conditions.[15] To produce pure hydrogen, biomass gasification must be followed by gas cleaning, water gas shift reaction, and hydrogen purification. An example of such separation system is presented in the schematic on Figure 2.

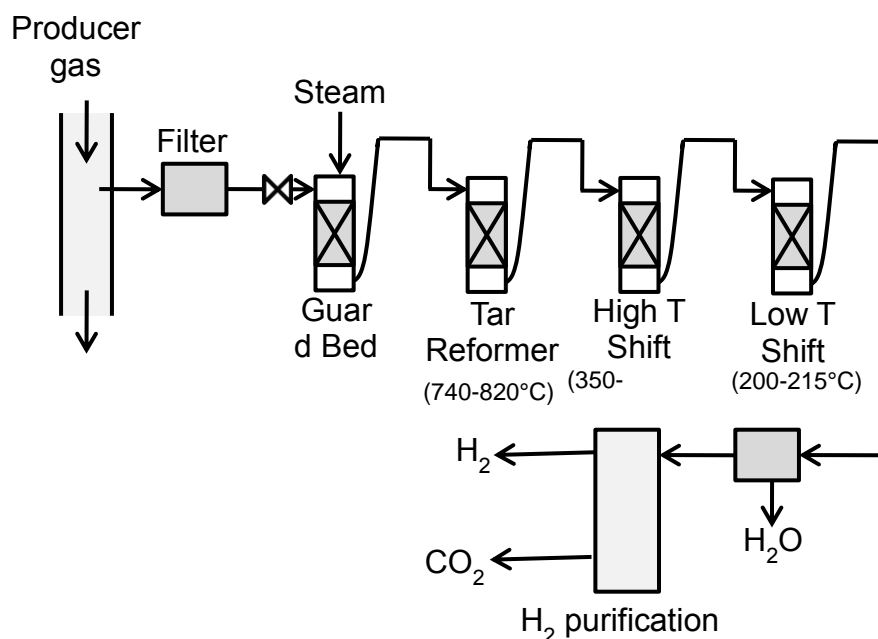
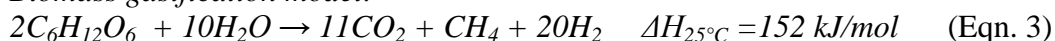


Figure 2. General schematic of system for clean hydrogen generation

A theoretical maximum hydrogen yield from biomass gasification can be approximated using glucose as model species assuming hydrothermal gasification [16]:

Biomass gasification model:



According to this equation a total of 2.0 L(gas)/g of biomass can be generated with approximately 62 %^{mol} H₂. In recent reports of laboratory experiments, gas yields from a simple batch-type steam gasifier have been reported at 0.5-1.1 L/g of biomass and hydrogen concentrations around 50-60 %^{mol} at temperatures ranging from 500-700°C.[18] Hydrogen concentrations in product gas from a CO₂ sorption enhanced steam gasifier have been reported above 60 %mol and gas yields around 1.4 L/g of biomass at temperatures between 500-700°C.[18,19] Results from a supercritical water biomass gasifier has been reported at

around 2.0 L/g of dry biomass (1.5 g/g) at 650°C and 22 MPa, where the hydrogen concentration was about 55% mol.[20] Clearly hydrothermal or gasification using supercritical water could help maximize the gas productivity. Challenges associated with this technology will be addressed later.

An important type of gasifier is the indirectly heated gasifier. In this case a steam-only gasification is preheated and run with high-temperature steam. These type of setups can generate a gas with high fraction of hydrogen while some of the reactions involved are endothermic, the latter being a factor said to improve thermal efficiency.[21] Because of this overall endothermicity these results are obtained at temperatures low enough where water-gas shift reactions become very important. It has been reported that steam only gasification generates more tars than oxygen-blown gasification. In the case of coal gasification this approach has been found to also have lower reactivity than gasification with oxygen so that a trade off can be identified.[22]

Concerns have been raised about the energy intensive step of biomass drying for gasification or liquefaction processes.[23] In steam and air blown gasifiers, air is added to introduce partial oxidation reactions which are highly exothermic and release heat that can be employed for the endothermic steps of drying as well as the pyrolysis reactions during gasification.[24] The next step of the gasification reaction involves solid carbon reactions. These include mainly carbon oxidation, the Boudouard reaction, steam reforming of carbon, and carbon hydrogenation. Some of these reactions are exothermic and others endothermic and the balance between these depends on a number of variables including gasification temperature and gas composition from the previous steps. The last step is defined as gas-phase reactions that adjust the final composition of the producer gas.

A supercritical water (SCW) gasifier design has been proposed to also deal with the energy cost of drying the biomass by completely eliminating the need for it. This type of operation may eliminate the need for a biomass drying step for biomass moisture levels up to 95% by weight. In this type of operation it can also be expected that by bringing the water to supercritical conditions the energy expenditure of vaporizing the water is reduced. This process has been investigated in the past by employing fixed bed reactors.[25,26] Reactor

plugging by char or ash buildup has been an important limitation in SCW gasification. A fluidized bed design was proposed to solve this issue.[23,27] Applying the commonly used fluid bed concept for a SCW biomass gasifier presents a series of unique challenges.

In the work by Lu et al., similar results in terms of hydrogen production were observed from fluidized supercritical water gasification when compared to a similar operation in a tubular reactor.[23] Hydrogen yields for these tests came up to be significantly lower than typical biomass gasification mainly due to the lower operation temperature underlining the critical importance of this parameter. Also the energy cost of biomass drying and grinding to small particle sizes also presents a limitation in the case of traditional gasification.

Another way to introduce heat indirectly is through a latent heat ballast as described by Pledka et al., to increase the thermal efficiency and heating value of producer gas from biomass up to 16.6 KJ/Nm³. [28,29] This approach takes advantage of indirectly heated gasification where combustion and pyrolysis processes are separated into stages within the same reactor vessel. In general terms, an indirectly heated gasifier is defined by when heat is generated during the exothermic combustion of either natural gas or biomass with air so that the excess heat is harnessed to be able to carry out the pyrolysis reactions of steam gasification.

A thermal ballast allows both stages to still be performed in a single reactor vessel with efficient operation even in small scales such as pilot scale fluid bed gasification. The thermal ballast has been tested as a series of tubes filled with non-corroding lithium fluoride salt. This material would phase transition close to the gasifier temperature operating range and thus storing latent heat from the combustion stages. Other approaches involving two separate vessels include the circulation of different types of heat carriers from a combustor into the gasification vessel [29], and heat transfer through a common wall between the two processes.[30] The single vessel design not only greatly reduces capital costs but allows for biomass to be introduced as the combustion fuel replacing the use of non-renewable natural gas.

As part of an effort to help mitigate the release and sequester CO₂, a system was proposed to utilize it as oxidizing agent for biomass gasification.[31,32] This type of gasification has proven to produce lower yields of gas with increased char and tar. However, the use of a catalyst looks promising for this kind of operation as it has been tested for char gasification. In the work by Hurley et al. this concept was tested in a batch gasification system with catalyst doped biomass. All of the metal ions introduced showed enhancement compared to regular CO₂ gasification at temperatures up to 800°C, metals added include Fe, Co, Ni, and Ru.

Gas cleaning

One of the challenges immediately associated with biomass gasification is the large amounts of liquid and gaseous co-products generated that need to be separated in order to obtain high purity syngas.[33] Other contaminants in the producer gas may include particulates, ammonia, sulfur containing gas, and hydrogen chloride. Tar, for example, represents a nuisance for downstream use of the producer gas as it may accumulate in filters, pipes, engines, and other surfaces where they reduce component performance. It is clear that before the raw producer gas mixture can be used it would need some polishing focusing primarily tar and sulfur removal.[34]

We could consider the removal of particulates as the primary gas cleaning step. This primary cleaning is typically performed by the use of cyclones or filters at the exit of the gasifier. Following cleaning steps like sulfur removal can be performed by water scrubbing. Water scrubbing can take care of some the halides and some of the tars. Tar removal remains the most challenging cleaning step to condition the producer gas to facilitate downstream processes.

Tar can be efficiently removed using physical separation methods like filtration or wet scrubbing. These methods will still require appropriate disposal of the material. It is also important to consider the thermal efficiency impact of having to cool down the gas stream prior to the physical separation step. Thermal and catalytic destruction of tars have been studied to crack them to useable gas products. It has been shown that in order to thermally

crack the tars efficiently they need to be heated to temperatures higher than 1000°C. In contrast, catalytic cracking of tars can be performed at temperatures as low as 600°C, avoiding the capital cost associated with specialized high temperature materials.[21]

Effective catalytic removal of tars from raw producer gas has been demonstrated with upwards of 99% success.[35] This removal was governed by the steam reforming of tars, thus converting the undesired species into hydrogen increasing its content in the producer gas. A nickel based catalyst (Ni/CaO/K₂O/SiO₂/Al₂O₃) loaded reactor has been operated at temperatures between 740-820 °C, and steam/TOC of 2.8.

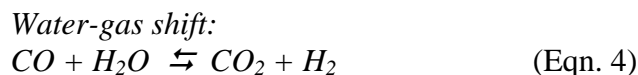
In this study by Zhang et al., the catalytic reactor was preceded by a gas pre-treatment vessel containing calcined dolomite as a guard bed.[35] The dolomite was intended to crack the heavier tars and to protect the metal catalyst from fouling and to extend its life. The catalytic reactor train was tested with a slip stream of producer gas coming from a pilot scale air blown gasifier.

The resulting concentration of hydrogen was increased by up to 11 vol% (dry basis). Materials like calcined dolomite have been used in an effort to trap sulfur species arising from the producer gas, however evidence shows very low sulfur capacity that leads to accumulation on the reforming catalysts. Although previous extensive testing has shown that steam has no effect on the sulfur chemisorption equilibrium on nickel catalysts [36], evidence of reduced accumulated sulfur was found with higher steam/TOC ratios. Further investigation could include validating the role of the dolomite bed on the gas composition and to perform stability studies of different synthesized reforming catalysts to correlate the results with specific catalytic phases or additives.

Water-gas shift

A water-gas shift (WGS) step can be included downstream of the gasifier or catalytic reformer to maximize the hydrogen yield from biomass. This reaction would convert the CO from the producer gas into CO₂ and additional hydrogen by consuming water vapor.[37,38] The WGS reaction is a current industrial process typically coupled with steam-methane

reforming and has been studied extensively [39-42]. This reaction would be advantageous since biomass gasification yields high amounts of CO relative to the H₂. The WGS reaction is typically performed by using a high temperature shift reactor (350-450 °C), and a secondary low temperature reactor (200-215 °C) due to this reaction being thermodynamically limited [43,44]. Further work on biomass producer gas polishing from Zhang et al. tested a system equipped with WGS reactors.[45] This system was an extension on the tar conversion system described previously [35], similar to the schematic on Figure 2. An example of the results possible with such a shift reactor system for syngas is presented on Table 1.



An extension of the work by Zhang et al. could show the cut off temperature for the efficient removal of tars and study the possibility of condensing the tar reforming and high-temperature shift vessels into one. It would be interesting to include as well the role of the guard bed which could also behave as a catalyst. Instead of using external stages for WGS a high-temperature shift catalyst can be used in a membrane reactor.[46,47]

Table 1. Gas Composition at Various Locations in the Gas Conditioning System (from [45])

	raw gas	outlet steam reformer	outlet high-temperature shift	outlet low-temperature shift
gas composition ^a				
H ₂	8.6 ± 0.2	19.4 ± 0.2	23.7 ± 0.1	26.7 ± 1.9
CO	14.3 ± 0.5	9.0 ± 0.2	1.4 ± 0.5	0.11 ± 0.04
CO ₂	18.0 ± 1.0	20.5 ± 0.2	26.8 ± 0.1	27.4 ± 0.03
CH ₄	4.5 ± 0.1	3.36 ± 0.02	3.1 ± 0.1	1.9 ± 0.9
C ₂ H ₄	1.5 ± 0.05	0.28 ± 0.01	0.08 ± 0.05	0.13 ± 0.08
CO shift conversion			83%	98.70%
tar content (g/Nm ³)	19.5	(b)	(b)	(b)

^a Gas composition is dry basis (vol-%) measured by gas chromatography. ^b No heavy tar by observation.

Maroño et al. showed the viability of adding a high-temperature Fe-Cr WGS catalyst to the gasifier to incorporate the two steps at operating temperatures below 500°C.[48] The type of gasifier used was an oxygen pressurized reactor. For this case it was found that the temperature and steam addition were critical parameters for the performance of the catalyst.

The use of this kind of shift catalyst still needs to be tested in an integrated operation to study the interaction of the WGS and the gasification reactions.

Syngas fermentation

Bioreactors can be coupled with gasifier systems to essentially perform the shift reaction while sequestering carbon from the syngas.[49] A test syngas fermentation system is presented in Figure 3. The CO can be utilized to grow bacteria under different sets of conditions. One microorganism of interest is the *Rhodospirillum rubrum*, which can grow by consuming CO as its only energy source under anaerobic conditions.[50] The biocatalytic activity of this bacterium results in the WGS reaction while some of the CO₂ generated is metabolized to produce polyhydroxyalkanoate (biopolymer PHA).

The *R. rubrum* is also conveniently capable of metabolizing sulfur in the form of H₂S, removing it from the gas stream. In this case it has the potential to eliminate costly separation steps to remove sulfur traces from the gas. One common limitation to this type of operation is the mass transfer of CO from the gas bubbles to the liquid for the organism to consume. To overcome this it is necessary to design a bioreactor capable of increasing the contact between the gas and the liquid (e.g. vigorous stirring, etc.).

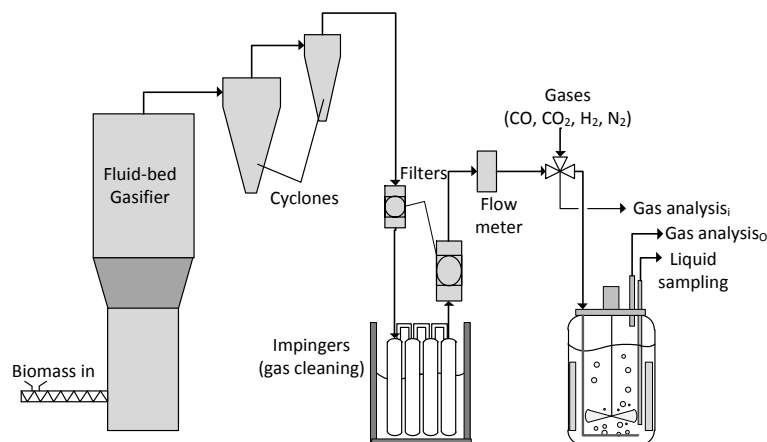


Figure 3. Schematic of gasifier coupled with syngas fermentation unit (simplified from [49])

It is necessary to consider the removal toxic species from the gas prior to the bioreactor. In laboratory reactors this has been easily achieved with in-line activated carbon filters.[49]

Pyrolysis of biomass

Biomass can be pyrolysed to produce a liquid product, pyrolytic char and non-condensable gas [51-53]. Fast pyrolysis is the thermal decomposition of biomass to recover liquids as the main product. During fast pyrolysis the feedstock is heated to moderate temperatures typically 375-525°C in the absence of oxygen and the vapors are quickly condensed before thermodynamic equilibrium is achieved. This way the intermediate products are recovered in liquid form. These liquids, commonly referred as bio-oil or fast pyrolysis liquids, can be treated as a highly oxygenated form of crude oil. Bio-oil contains roughly 10 times higher energy density than biomass making it an easier to transport energy carrier.

The fast pyrolysis process concentrates most of the chemical energy contained in bulky biomass into a denser liquid form.[51,52,54,55] Compared to gasification and combustion, fast pyrolysis has the advantage of producing an intermediate energy carrier that can be stored and transported economically, so that the upstream biomass conversion and the downstream processing of bio-oil can be carried out at different locations, times and scales. This approach gives the opportunity to take advantage of the economies of scale.

The bio-oils can be obtained in yields higher than 70% of dry biomass weight as a mixture of compounds derived from cellulose, hemi-cellulose and lignin found in biomass.[56,57] Bio-oils are mixtures that can contain hundreds of different compounds. They are composed of very complex mixtures of carboxylic acids, sugars, alcohols, aldehydes, ketones, esters, furan compounds, and aromatics.[52,58,59] The complexity is derived from the degradation and interaction of the cellulose, hemicellulose and lignin products. The bio-oils are present as a liquid mostly because of the water content which ranges in most cases between 15 to 25%. Its composition varies depending on a large number of variables like type of biomass feedstock, alkali content, reactor type, pyrolysis temperature, vapor residence time, efficiency of char removal, etc.[51,60,61]

Fast pyrolysis of biomass to produce bio-oil has already reached some level of commercial availability.[62] Due to the high oxygen content, high water content, and chemical instability of bio-oils they are not currently considered fuels themselves.[63] Upgrading is necessary to meet fuel specifications and demands. Some of the main challenges associated with bio-oil utilization include: high cost of the liquid, the fact that they are not compatible with conventional fuels, and the lack of defined quality standards as well as transportation and handling standards.[3,51]

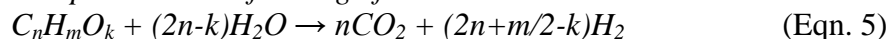
Bio-oil steam reforming

Bio-oil represents an intermediate product suitable for upgrading to liquid fuels and also considered as an energy and hydrogen carrier. The bio-oil could be generated in a distributed manner, transported to a centralized biorefinery and upgraded to a series of products.

Hydrogen can be obtained by steam reforming whole or water-soluble fractions of bio-oil. If the water-gas shift reaction is taken into account, high-yields of clean hydrogen and CO₂ can be obtained. One of the advantages of bio-oil steam reforming process when compared to biomass gasification is the fact that no tar is generated thus eliminating the need to extensive gas cleaning processes. Another advantage of the catalytic process is related to avoiding the capital cost of specialized materials required for gasifiers that operate at very high temperatures. A number of factors and challenges need to be carefully addressed in order to optimize the efficiency of this process.

The high level of oxygenation of the species found in bio-oils makes them more reactive when compared to traditional steam reforming feedstock like hydrocarbons.[59,64] In spite of this some amount of important research in bio-oil reforming has been performed based at the usual conditions for hydrocarbon reforming.[59,65,66] Plus at the lower temperature range both SR and WGS reactions can be performed simultaneously in the same operation.[67] Equation 5(Eqn. 5) shows the complete steam reforming to hydrogen and carbon dioxide, where n, m, and k represent the empirical formula of the bio-oil as obtained by elemental analysis.

Complete steam reforming of bio-oil:



The bio-oil separates into water rich carbohydrate derived phase and a hydrophobic oligomeric phase by simple water addition.[56] The bio-oil aqueous phase is light brown liquid composed by about 84% water and mostly hydrophilic low molecular weight oxygenated compounds. It is characterized by the presence of carboxylic acids such as acetic and formic acids, aldehydes, ketones, alcohols, esters and others. The water insoluble fraction of the bio-oil is separated as a valuable material [68] that could be directly refined or upgraded to specialty chemicals and additives,[51,69] while the aqueous fraction could be steam reformed to generate hydrogen.

Wang *et al.* employed an advanced triple-nozzle spraying system to introduce the aqueous bio-oil fraction into a fixed bed reformer.[68] The chemical composition of this bio-oil was not presented. At 700°C the stoichiometric H₂ yields averaged 83 % mol and with more carbon deposition than model compounds studied. In the work by Rioche *et al.* whole bio-oil was reformed by using a variety of catalysts.[66] The production of H₂ was not very stable with a hydrogen stoichiometric yield less than 70 %mol at the intermediate temperatures tested (T=795°C). The bio-oil in this case was produced from beech wood fast pyrolysis.

Kechagiopoulos *et al.* reported that hydrogen yield from aqueous bio-oil did not surpass 56 mol % of the stoichiometric potential at temperatures from 600-900°C over commercial Ni-based catalyst.[64] In this case the bio-oil was obtained from catalytic pyrolysis of beech wood. Chemical composition of bio-oils tested is not typically presented. The reforming of bio-oil aqueous phase seemed very different from reforming of the selected model compounds. The main reason for this was higher carbon deposition decreasing the catalyst stability and limiting the hydrogen potential. Also the nature of the carbon deposits was briefly studied.

A series of tests using different combinations of noble metal catalysts and different types of support structures was completed to study their SR performance in laboratory scale reactors. For example, a research group from CenTACat in the University of Belfast in Ireland reported the performance of high-cost noble metal catalysts such as Pt, Pd, Rh oxides which

were impregnated on two different types of supports, like alumina (Al_2O_3) and ceria-zirconia (CeZrO_2). [66] Reasons why noble metal catalyst would be a good choice are based on the possible advantages over a Ni-based catalyst such as better selectivity to hydrogen instead to coke formation when reforming the whole bio-oil, and possible higher activity per unit volume of metal based on its ability to perform dehydrogenation reactions. Four model compounds were reformed [66] to test the effect of metal catalyst and also the effect of the nature of the support and find a versatile combination for bio-oil SR. Acetic acid was used to model the carboxylic acids, phenol to model the phenolics from lignin, acetone to model the carbonyl containing ketones and aldehydes, and ethanol to model the alcohols based on a carbon oxides (CO and CO_2) yield from total carbon input. The Rh supported over alumina performed better for all selected model compounds than the other formulations. The hydrogen yield based on stoichiometry of the model compounds was higher for the Rh- CeZrO_2 .

Some of these catalyst formulations have been also tested using real bio-oil (from beech wood pyrolysis supplied by the University of Twente). [66] This bio-oil containing both the hydrophobic and the hydrophilic fraction was co-fed with water to the reactor by using two separate syringe pumps. In this case, the catalyst formulations using noble metals over ceria-zirconia supports showed high yields and conversion to gas products at temperatures above 740°C . There was no clear effect of catalyst metal selection compared to the effect found by the support for full bio-oil reforming. A bifunctional mechanism can be proposed for some of the oxygenated present in bio-oil over noble-metal catalysts where (similarly to methane reforming on supported Ni catalysts) these are activated on the metal sites and the steam activated on the support. The increased activity observed over ceria-zirconia could be associated with the redox properties of this material.

As shown in previous experiments by Wang *et al.* a fixed-bed reactor would perform well but the activity was affected within hours. [68] The use of a fluidized bed was proposed by Czernik *et al.* [59,70] to improve the performance of the reactor by providing good contact of the catalyst with the reactants and shearing off carbonaceous deposits, thus potentially increasing the times on stream. The main goal of this work was to attempt to improve

catalyst stability. Other issues were found for this kind of setup adding to the complexity of the tests, for example, the catalyst used lacked the mechanical strength necessary resulting in high attrition losses. Attempts were made to make the catalysts stronger mostly at the expense of losing measurable catalytic activity.

Several approaches have been tested previously employing specialized noble metal catalysts and special reactor arrangements like fluid beds and sequential bio-oil gasification and reforming operations. It is clear that because of the chemical complexity of the bio-oils, from fast pyrolysis of biomass, it is difficult to study in depth the causes for low hydrogen yields and poor catalyst stability. More systematic approaches are needed to try to understand the specific sources or pathways of these issues to be able to mitigate them.

Autothermal reforming

In order to minimize carbon deposition during SR of bio-oil, it has been proposed that a small stream of oxygen is introduced in what is commonly known as autothermal operation. The oxygen addition to the SR reaction introduces exothermic partial oxidation reactions that can allegedly help remove carbon deposits during the operation. The premise was that a small concentration of oxygen would not negatively affect the hydrogen yield from oxygenated compounds. The autothermal operation should also provide important amounts of heat that could help reduce the operation cost of the reformer. The benefits of this kind of operation would clearly be maximized in a highly heat-integrated large scale operation.

In the work by C. Rioche in Ireland [66], the results showed a significant reduction of carbon deposition in the reactor when oxygen was introduced during whole bio-oil SR over a Pt-ceria/zirconia catalyst. Substantial hydrogen yield decrease was also observed as the concentration of oxygen was increased. Severe catalyst deactivation over time was also detected with the addition of oxygen when compared to the SR alone. This deactivation could be attributed to catalyst sintering because of extremely high temperatures achieved locally during highly exothermic oxidation reactions on the metal. This presents a challenge then in designing a catalyst that is more stable under extreme conditions and possibly the need for a water-gas shift reactor to be able to maximize hydrogen productivity. For this case

the decrease in hydrogen yields and severe deactivation issues counterweight the improvement in coke deposition and essentially discourages the autothermal approach in bio-oil reforming.

Bio-oil gasification

Hydrogen production via bio-oil gasification has been briefly studied as an alternative to steam reforming.[71] The producer gas obtained from biomass gasification is of relatively low calorific value, which limits the options for its utilization. Cleaner producer gas, than currently obtainable from biomass gasification, is needed for applications in combustion and fuel cells. Bio-oil is a cleaner intermediate product that densifies the biomass energy potentially making it easier to transport and process. The bio-oil liquids can then be gasified at a centralized facility taking advantage of the economies of scale.[72]

Early bio-oil gasification experiments at small scales with temperatures between 650 and 800°C over inert fixed beds yielded product gases where hydrogen was not the main product.[73] These experiments lacked the basic addition of steam or air for gasification which could have potentially hindered the results. The product gas in these cases was considered for its high heating value (between 1300 and 1700 Btu/SCF) based on the amount of methane, ethylene, hydrogen and carbon monoxide among smaller portions of higher hydrocarbons.

Steam gasification of crude bio-oil has been investigated at temperatures around 800°C as a pretreatment for catalytic steam reforming for hydrogen production.[71] Bio-oil steam gasification is characterized by the use of inert material and high temperatures to thermally decompose the organic species. The purpose of this step in this case was to help mitigate the coking on a downstream catalytic reactor. Results from the bio-oil gasification showed a higher H₂ yield as the reactor temperature increased but the values were capped at about 30 % of the stoichiometric potential at S/C of 10.6 and GHSV (gas hourly space velocity based) equal to 7810 hr⁻¹. Significant amounts of hydrocarbon gases (mostly C₁-C₃s) as well as condensable organics (mostly C₅-C₇) and tars (C₈₊) have been detected during these tests. The amount of these species was significantly reduced when comparing to the crude bio-oil

before gasification especially at the higher gasification temperatures. Other species like phenol appeared to be concentrated after gasification at 500°C but similarly converted at the higher temperatures.

For the combination of type of bio-oil and catalyst (NiCuZnAl) used for these tests, direct catalytic reforming resulted in rapid deactivation and high carbon deposition at the expense of H₂ yield (at conditions: T = 700°C, S/C = 10.6). The combination of steam gasification and catalytic reforming gave improved results with H₂ yields around 65 % when the temperatures were 800°C and 700°C respectively. Carbon deposition was reduced by about an order of magnitude after 2hr of time on stream. Higher hydrogen yields up to 81% of the stoichiometric maximum (Eqn. 6) were obtained when the reforming reactor was operated as an electro-chemical catalytic reformer as part of the integrative process. Catalytic reduction by electron current over the catalyst is a possible contributor for these results but also the fact that the electrical wires inducted higher localized temperatures registered well above the average bed temperatures. Energy input calculations render the current-enhanced process more efficient than the gasification and conventional steam reforming combination. This is in harmony with the observation that the current wire generates important heat for the reaction, and that the heating induced by the current may be more efficient than the heating from the external heating elements.

Hydrogen stoichiometric yield:

$$Y_{H_2} = \frac{\text{moles of } H_2 \text{ obtained}}{\text{moles of } H_2 \text{ stoichiometric potential}} \quad (\text{Eqn. 6})$$

It is important to note that the overall reaction of steam and bio-oil to H₂ and CO₂ is endothermic regardless of the reaction system used. Gasification or pyrolysis of bio-oil pretreatments at lower temperatures and lower energy intensive could prove a more efficient manner to mitigate coking issues and need to be investigated. Addition of small amounts of air that could be mostly consumed during the gasification stage could be beneficial for the overall energy balance potentially without greatly compromising the hydrogen yield.

A two bed concept has been tested as well by van Rossum et al., where the bio-oil was pretreated in a fluidized bed gasifier and then steam reformed in a fixed bed catalytic reactor.[74] This approach has the potential of thinning the chances of catalyst attrition losses typical of fluid bed reformers. A two-bed concept, using a fluid sand bed followed by a catalytic bed results in hydrocarbon free and low tar gas with an estimated hydrogen yield of 0.14 kg H₂/kg of dry biomass.

Biomass depolymerization by hydrolysis

A process like acid and hydrolysis could be used to generate primarily sugar monomers from biomass.[75] Biomass depolymerization to sugars can be performed mainly via dilute acid, concentrated acid and enzymatic hydrolysis. Acid hydrolysis, either with a dilute or concentrated acid, can convert the cellulose and hemicelluloses of biomass leaving the lignin behind. The enzymatic hydrolysis pathway requires pretreatment of the biomass to separate into cellulose, hemicelluloses and lignin.[76]

The highest glucose yields from concentrated acid hydrolysis can be obtained up to 90%.[77] Concentrated acid hydrolysis usually involves large volumes ratios of concentrated H₂SO₄ to biomass and the recovery of the acid for reuse is not trivial. The acid in this case will need to be neutralized thereafter.

Dilute acid hydrolysis employs a much more dilute acid (about 10 times less concentrated) and slightly elevated temperatures and pressures. Glucose yields from dilute acid hydrolysis of biomass have been reported at around 50 %.[78] The higher temperatures accelerate the hydrolysis but introduce a level of decomposition in the case of hemicelluloses as well as heat transfer limitations.

An enzymatic hydrolysis process is attractive based on enzyme specificity which can eliminate the waste stream generated via acid hydrolysis and the need to treat the liquid stream. Cellulose crystallinity, lignin and hemicellulose protection are all important factors that contribute to the resistance of biomass to enzymatic hydrolysis. Biomass pretreatment strategies tested include hot water methods and ammonia fiber expansion.[79,80]

Unfortunately the cost of the enzyme used is currently projected to be an important bottleneck for this kind of process. Other issues include slow turnover rates and low thermal stability inherent to enzymes.

Another kind of hydrolysis is the alkaline hydrolysis.[81] This is a fast reaction process but can lead to degradation reactions and leading to the formation of acids like lactic acid. For this reason alkali hydrolysis has been suggested more suitable as a pretreatment for biomass to perform subsequent enzymatic hydrolysis.

An alternative process that has been demonstrated is the catalytic depolymerization of cellulose in ionic liquids.[82,83] These ionic liquids are specialty materials that are able to solubilize cellulose under mild conditions and provide a medium for catalytic processing. However ionic liquid strategies have to deal with high cost of materials and extensive separation processes which provide no clear advantage when compared for example to concentrated acid hydrolysis. Also this has only been demonstrated for the cellulose component which would have to be obtained by a pretreatment of the biomass.

Aqueous phase processing of carbohydrates

Hydrogen then can be produced via condensed phase catalytic conversion of sugars and sugar alcohols using supported metal catalysts. These reactions similarly to the steam reforming involve the breaking of C-C, C-H and OH bonds. The main products from these condensed phase reforming reactions are H₂, CO₂, CO, and some light alkanes. Conditions for such a process are in the moderate range of temperature slightly above 200 °C and elevated pressures (above 10 bar) enough to keep the water in the liquid phase.[84]

Davda et al. proposed the use of an aqueous phase reforming (APR) as a condensed phase reaction for the production of hydrogen from biomass derived feedstocks like carbohydrates and alcohols.[85] A Pt/SiO₂ catalyst showed high selectivity to H₂ from ethylene glycol as a model compound, compared to Ni or Ru based materials which promoted the formation of undesired light alkanes to a larger extent. Alumina supports have also shown good qualities in this reaction.[86]

Further work was done by introducing a series of Pt and Ni based catalyst materials including a Sn modified Raney-Ni catalyst to produce hydrogen from ethylene glycol, sorbitol, and glycerol.[87] The conditions for these tests were 225 – 265 °C and pressures 26 – 56 bar. Reforming experiments were performed under transport effect-free conditions. The results showed that the Raney-NiSn catalyst was able to achieve high activity levels similar to those found for the Pt/Al₂O₃ catalyst. The selectivity found from this catalyst formulation surpassed those of the unmodified Raney-Ni catalyst. The Sn promoted catalyst seemed to discourage the methanation reaction without negatively affecting the hydrogen yields. With this catalyst the hydrogen selectivity seemed to decrease with increasing alkane formation as the pressure was increased thus conditions near the bubble point of the feed solution seem to be favorable for hydrogen production.

A clear advantage of such process comes from the fact that the carbohydrate feedstocks are stable upon storage when compared to bio-oils. Selectivity issues have been a consistent challenge with these condensed phase reactions. Even though the gas product distributions for these processes can vary greatly with the model species used the alkane formation seems to be inevitable. Generally low turnover rates are also a characteristic of condensed phase stirred reactions as opposed to flow reactors. Long term stability seems to be another issue with plenty of the catalyst tested where significant deactivation occurred in about the first 10 hr of reaction.[87]

Challenges

The first question that needs to be addressed is about the availability of biomass and the ability to transport it for hydrogen or biofuel production. The availability and variety will definitely depend on a series of regional factors [63]. It is encouraging that biomass in many instances like in the case of agricultural wastes are free and abundant. However one big hurdle in obtaining hydrogen from the biomass gasification scheme lies in the transportation of biomass to centralized processing units, but this may present opportunities to focus on smaller scale distributed operation. [72]

Gasification of biomass is attractive since it allows the use of robust and well developed technology similar to coal gasification. The combustible gas mixture from the gasifier needs to be extensively refined or polished to generate clean syngas which then can be converted to hydrogen and carbon dioxide via a catalytic process like WGS. This gas cleaning step is extremely important since the downstream catalysts can be poisoned very easily compromising stability and performance.

The fast pyrolysis of biomass is considered generally a less expensive technology compared to biomass gasification which requires extensive heat integration and expensive construction materials suited for the elevated temperatures. For this reason it is very important to consider bio-oil as a hydrogen/energy carrier or intermediate product for the production hydrogen. The study of bio-oil SR is complex since some of the compounds found in bio-oils would require different types of catalysts and operating conditions.[64] SR of bio-oil is characterized with all the difficulties typical for most hydrocarbon reforming processes. These difficulties include high operating temperatures. Heat needed for the endothermic reactions, and above all the formation of carbon deposits which not only sacrifices an amount of hydrogen that could be produced but limits the time on stream. Steam reforming of bio-oil presents special challenges coming from the chemical diversity and complexity of bio-oils.

Bio-oils may always require special handling or upgrading because of its non-volatility and tendency to polymerize upon heating at temperatures about 80 °C and at higher temperatures they start to decompose.[88] As in all catalytic reactions the catalytic approaches mentioned need to include efforts in the development of inexpensive catalysts that are highly active and with good long term stability. This concept of stability is generalized to also include the non-catalytic processes as solid accumulations and slag can occur considering the amount of inorganics present in the original biomass. It must be noted also that little evidence has been presented of long term stability for both the catalytic and non-catalytic processes like gasification, pyrolysis, reforming, etc.

Strategies that involve biomass depolymerization by hydrolysis require expensive materials like concentrated acids and enzymes and the subsequent separation of these is never trivial. Pretreatment methods have been presented and can alleviate some recalcitrance issues of

biomass but there are plenty of opportunities to keep improving these technologies to make sugars from biomass available for processing.

Aqueous phase processing of biomass derived molecules like sugars also presents an interesting approach providing opportunities for catalysis research. Selectivity issues like for example towards production of light alkanes will need to be addressed as well as efforts to improve turnover rates inherent to condensed phase reactions. The aqueous phase processing approach is a novel strategy and has been demonstrated only in laboratory scales and it would be likely that it will present up-scaling issues in the future together with more opportunities for development.

Conclusions

The production of hydrogen from renewable biomass presents a more carbon neutral generation of fuels and chemicals as opposed to petroleum feedstocks. Biomass is a sustainable resource since it can always be regrown. Hydrogen can be generated utilizing different types of technologies mainly derived from our knowledge on fuel production from crude-oil. In order to consider hydrogen as an alternative fuel it is important to consider that there is no infrastructure in place for the handling of hydrogen gas. However hydrogen is a valuable chemical in present fuel refining and upgrading and so will be in the case of a biorefinery especially when we consider the need to deoxygenate bio-based molecules to produce more energy dense fuels and compatible with the present infrastructures.

Some recent findings were summarized together with brief descriptions of technical challenges and hurdles found in these processes. Some of the main challenges have to do with producer gas cleaning and polishing, biomass handling and catalyst stability issues. A lot of the research in these areas relies heavily on academic research but efforts are being clearly put by large and small companies to bring these technologies to commercial scales. These technologies as applied to the conversion of biomass are still in their development stages and with driving forces like environmental awareness and regulations for clean fuels they would soon be mature enough to reach production scales based over solid fundamental knowledge.

References

1. Chornet E, Czernik S: Renewable fuels: Harnessing hydrogen. 418(6901), 928-929 (2002).
2. Garcìa-Pèrez M, Chaala A, Roy C: Vacuum pyrolysis of sugarcane bagasse. *Journal of Analytical and Applied Pyrolysis* 65(2), 111-136 (2002).
3. Bridgwater AV: Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal* 91(2-3), 87-102 (2003).
4. Dalcór, Camford: Canadian hydrogen survey - 2004/2005. A study conducted for Natural Resources Canada by Dalcór Consultants Ltd and Camford Information Services.
5. Levin DB, Chahine R: Challenges for renewable hydrogen production from biomass. *International Journal of Hydrogen Energy* In Press, Corrected Proof,
6. Gustavsson L, Börjesson P, Johansson B, Svanbergsson P: Reducing CO₂ emissions by substituting biomass for fossil fuels. *Energy* 20(11), 1097-1113 (1995).
7. Hall DO, House JJ: Biomass: A modern and environmentally acceptable fuel. *Solar Energy Materials and Solar Cells* 38(1-4), 521-542 (1995).
8. Brown RC: Biorenewable resources : engineering new products from agriculture. Iowa State Press, Ames, Iowa. (2003).
9. United states department of energy (US DOE). Central hydrogen production via biomass gasification, http://www.Hydrogen.Energy.Gov/h2a_prod_studies.html,
10. Higman C, Burgt MVD: Gasification. (2nd). Gulf Professional Pub./Elsevier Science, Amsterdam ; Boston. (2008).
11. Balat M, Balat M, Kirtay E, Balat H: Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Conversion and Management* 50(12), 3147-3157 (2009).
12. Berkowitz N: An Introduction to Coal Technology. (2nd ed). Academic Press, New York. 282-337 (1994).
13. Ni M, Leung DY, Leung MKH, Sumathy K: An overview of hydrogen production from biomass. *Fuel Processing Technology* 87(5), 461-472 (2006).
14. Demirbas MF, Balat M, Balat H: Potential contribution of biomass to the sustainable energy development. *Energy Conversion and Management* 50(7), 1746-1760 (2009).
15. Satrio JA, Shanks BH, Wheelock TD: A combined catalyst and sorbent for enhancing hydrogen production from coal or biomass. *Energy & Fuels* 21(1), 322-326 (2007).
16. Schmieder H, Abeln J, Boukis N *et al.*: Hydrothermal gasification of biomass and organic wastes. *The Journal of Supercritical Fluids* 17(2), 145-153 (2000).
17. Muradov NZ, Veziroglu TN: "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies. *International Journal of Hydrogen Energy* 33(23), 6804-6839 (2008).
18. Mahishi MR, Goswami DY: An experimental study of hydrogen production by gasification of biomass in the presence of a CO₂ sorbent. *International Journal of Hydrogen Energy* 32(14), 2803-2808 (2007).
19. Wei L, Xu S, Liu J, Liu C, Liu S: Hydrogen Production in Steam Gasification of Biomass with CaO as a CO₂ Absorbent. *Energy & Fuels* 22(3), 1997-2004 (2008).

20. Antal MJ, Allen SG, Schulman D, Xu X, Divilio RJ: Biomass Gasification in Supercritical Water. *Industrial & Engineering Chemistry Research* 39(11), 4040-4053 (2000).
21. Umeki K, Yamamoto K, Namioka T, Yoshikawa K: High temperature steam-only gasification of woody biomass. *Applied Energy* 87(3), 791-798
22. Kajitani S, Hara S, Matsuda H: Gasification rate analysis of coal char with a pressurized drop tube furnace. *Fuel* 81(5), 539-546 (2002).
23. Lu YJ, Jin H, Guo LJ, Zhang XM, Cao CQ, Guo X: Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor. *International Journal of Hydrogen Energy* 33(21), 6066-6075 (2008).
24. Brown RC: Biorenewable resources : engineering new products from agriculture. (1st). Iowa State Press, Ames, Iowa. 146-148 (2003).
25. Fang Z, Minowa T, Fang C, Smith JRL, Inomata H, Kozinski JA: Catalytic hydrothermal gasification of cellulose and glucose. *International Journal of Hydrogen Energy* 33(3), 981-990 (2008).
26. Resende FLP, Neff ME, Savage PE: Noncatalytic Gasification of Cellulose in Supercritical Water. *Energy & Fuels* 21(6), 3637-3643 (2007).
27. Matsumura Y, Minowa T: Fundamental design of a continuous biomass gasification process using a supercritical water fluidized bed. *International Journal of Hydrogen Energy* 29(7), 701-707 (2004).
28. Pletka R, Brown RC, Smeenk J: Indirectly heated biomass gasification using a latent heat ballast. Part 2: modeling. *Biomass and Bioenergy* 20(4), 307-315 (2001).
29. Pletka R, Brown RC, Smeenk J: Indirectly heated biomass gasification using a latent heat ballast -- 1: experimental evaluations. *Biomass and Bioenergy* 20(4), 297-305 (2001).
30. Iliuta I, Leclerc A, Larachi F: Allothermal steam gasification of biomass in cyclic multi-compartment bubbling fluidized-bed gasifier/combustor - New reactor concept. *Bioresource Technology* 101(9), 3194-3208 (2010).
31. Hurley S, Li H, Xu C: Effects of impregnated metal ions on air/CO₂-gasification of woody biomass. *Bioresource Technology* (2010), DOI: 10.1016/j.biortech.2010.06.123
32. Roberts DG, Harris DJ: Char gasification in mixtures of CO₂ and H₂O: Competition and inhibition. *Fuel* 86(17-18), 2672-2678 (2007).
33. Guoxin H, Hao H: Hydrogen rich fuel gas production by gasification of wet biomass using a CO₂ sorbent. *Biomass and Bioenergy* 33(5), 899-906 (2009).
34. Verenum JG, Ventress L, Knoef H, Zielke U, Hansen PL, et al. Sampling and Analysis of tar and particles in biomass producer gases, <http://www.tarweb.net>,
35. Zhang R, Brown RC, Suby A, Cummer K: Catalytic destruction of tar in biomass derived producer gas. *Energy Conversion and Management* 45(7-8), 995-1014 (2004).
36. Rostrup-Nielsen JR: Some principles relating to the regeneration of sulfur-poisoned nickel catalyst. *Journal of Catalysis* 21(2), 171-178 (1971).
37. Ruettinger WF, Ilinich O: Water Gas Shift Reaction (WGSR). *Encyclopedia of Chemical Processing*, 3205 - 3215 (2005).

38. United states department of energy (US DOE). Fuel cell technologies program, https://www1.eere.energy.gov/hydrogenandfuelcells/production/natural_gas.html,
39. Carbo MC, Boon J, Jansen D *et al.*: Steam demand reduction of water-gas shift reaction in IGCC power plants with pre-combustion CO₂ capture. *International Journal of Greenhouse Gas Control* 3(6), 712-719 (2009).
40. Rhodes C, Hutchings GJ, Ward AM: Water-gas shift reaction: finding the mechanistic boundary. *Catalysis Today* 23(1), 43-58 (1995).
41. Tang Z, Kim S-J, Reddy GK, Dong J, Smirniotis P: Modified zeolite membrane reactor for high temperature water gas shift reaction. *Journal of Membrane Science* 354(1-2), 114-122 (2010).
42. Ratnasamy C, Wagner JP: Water Gas Shift Catalysis. *Catalysis Reviews: Science and Engineering* 51(3), 325 - 440 (2009).
43. Pasel J, Samsun RC, Schmitt D, Peters R, Stolten D: Test of a water-gas-shift reactor on a 3 kWe-scale--design points for high- and low-temperature shift reaction. *Journal of Power Sources* 152, 189-195 (2005).
44. Czuppon TA, Knez SA, Newsome DS: Hydrogen. *Encyclopedia of Chemical Technology* 13, 852-859 (1995).
45. Zhang R, Brown RC, Suby A: Thermochemical Generation of Hydrogen from Switchgrass. *Energy & Fuels* 18(1), 251-256 (2003).
46. Haryanto A, Fernando S, Adhikari S: Ultrahigh temperature water gas shift catalysts to increase hydrogen yield from biomass gasification. *Catalysis Today* 129(3-4), 269-274 (2007).
47. Enick R, Morreale B, Hill J *et al.*: Evaluation and Modeling of a High-temperature, High-pressure, Hydrogen Separation Membrane for Enhanced Hydrogen Production from the Water-gas Shift Reaction. In: *Advances in Hydrogen Energy*, 93-110 (2000).
48. Maroño M, Sánchez JM, Ruiz E: Hydrogen-rich gas production from oxygen pressurized gasification of biomass using a Fe-Cr Water Gas Shift catalyst. *International Journal of Hydrogen Energy* 35(1), 37-45
49. Do YS, Smeenk J, Broer KM *et al.*: Growth of *Rhodospirillum rubrum* on synthesis gas: Conversion of CO to H₂ and poly- β -hydroxyalkanoate. *Biotechnology and Bioengineering* 97(2), 279-286 (2007).
50. Kerby RL: Carbon monoxide-dependent growth of *Rhodospirillum rubrum*. *Journal of bacteriology* 177(8), 2241 (1995).
51. Huber GW, Iborra S, Corma A: Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 106(9), 4044-4098 (2006).
52. Bridgwater AV, Cottam M-L: Opportunities for Biomass Pyrolysis Production and Upgrading. *Energy & Fuels* 6(2), 113-120 (1991).
53. Mohan D, Pittman CU, Steele PH: Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* 20(3), 848-889 (2006).
54. J.G. B, A.V. B: Drying technologies for an integrated gasification bio-energy plant. *Renewable and Sustainable Energy Reviews* 3, 243-289
55. Badger PC, Fransham P: Use of mobile fast pyrolysis plants to densify biomass and reduce biomass handling costs--A preliminary assessment. *Biomass and Bioenergy* 30(4), 321-325 (2006).

56. Garcia L, French R, Czernik S, Chornet E: Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Applied Catalysis A: General* 201(2), 225-239 (2000).
57. Radlein D, Piskorz J, Scott DS: Fast pyrolysis of natural polysaccharides as a potential industrial process. *Journal of Analytical and Applied Pyrolysis* 19, 41-63 (1991).
58. Radlein D: The production of chemicals from fast pyrolysis bio-oils. In: Fast pyrolysis of biomass: A handbook, Al. AVBE. Newbury, UK: CPL Press, (1999).
59. Czernik S, Evans R, French R: Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catalysis Today. Recent Advances in Catalytic Production of Hydrogen from Renewable Sources* 129(3-4), 265-268 (2007).
60. Demirbas A: The influence of temperature on the yields of compounds existing in bio-oils obtained from biomass samples via pyrolysis. *Fuel Processing Technology* 88(6), 591-597 (2007).
61. Brown RC, Radlein D, Piskorz J: Pretreatment processes to increase pyrolytic yield of levoglucosan from herbaceous feedstocks. *ACS Symposium Series*, (2001).
62. Dynamotive energy systems. The Evolution of Energy,
<http://Www.Dynamotive.Com/Technology/>,
63. Tanksale A, Beltramini JN, Lu GM: A review of catalytic hydrogen production processes from biomass. *Renewable and Sustainable Energy Reviews* 14(1), 166-182 (2010).
64. Kechagiopoulos P.N., Voutetakis S., Lemonidou A., I AV: Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-oil in a Fixed Bed Reactor. *Energy and Fuels* (20), 2155-2163 (2006).
65. Markevich M, Czernik S, Chornet E, Montane D: Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil. *Energy Fuels* 13(6), 1160-1166 (1999).
66. Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R: Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Applied Catalysis B: Environmental* 61(1-2), 130-139 (2005).
67. Wang D, Montane D, Chornet E: Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde. *Applied Catalysis a-General* 143(2), 245-270 (1996).
68. Wang DN, Czernik S, Chornet E: Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. *Energy & Fuels* 12(1), 19-24 (1998).
69. Kechagiopoulos P., E. Vagia, A. Iordanidis, S. S. Voutetakis, A.A. Lemonidou, Vasalos IA: Hydrogen production from renewable energy sources: reforming of biogas and bio-oil. *Catalysis, Energy and Environment. Workshop of CPERI*, (2004).
70. Galdamez JR, Garcia L, Bilbao R: Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni-Al Catalysts. Acetic Acid as a Model Compound. *Energy Fuels* 19(3), 1133-1142 (2005).
71. Kan T, Xiong J, Li X *et al.*: High efficient production of hydrogen from crude bio-oil via an integrative process between gasification and current-enhanced catalytic steam reforming. *International Journal of Hydrogen Energy* 35(2), 518-532 (2010).

72. Wright M, Brown RC: Establishing the optimal sizes of different kinds of biorefineries. *Biofuels, Bioproducts and Biorefining* 1(3), 191-200 (2007).
73. Panigrahi S, Chaudhari ST, Bakhshi NN, Dalai AK: Production of Synthesis Gas/High-Btu Gaseous Fuel from Pyrolysis of Biomass-Derived Oil. *Energy & Fuels* 16(6), 1392-1397 (2002).
74. Van Rossum G, Kersten SRA, Van Swaaij WPM: Catalytic and Noncatalytic Gasification of Pyrolysis Oil. *Industrial & Engineering Chemistry Research* 46(12), 3959-3967 (2007).
75. Karimi K, Kheradmandinia S, Taherzadeh MJ: Conversion of rice straw to sugars by dilute-acid hydrolysis. *Biomass and Bioenergy* 30(3), 247-253 (2006).
76. Brown RC: Biorenewable resources : engineering new products from agriculture. Iowa State Press, Ames, Iowa. (2003).
77. Yu Y, Lou X, Wu H: Some Recent Advances in Hydrolysis of Biomass in Hot-Compressed Water and Its Comparisons with Other Hydrolysis Methods. *Energy & Fuels* 22(1), 46-60 (2007).
78. *Organic chemicals from biomass*. Goldstein IS. CRC Press, Boca Raton, FL (1981).
79. Mosier N, Wyman C, Dale B *et al.*: Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology* 96(6), 673-686 (2005).
80. Kim Y, Hendrickson R, Mosier NS *et al.*: Enzyme hydrolysis and ethanol fermentation of liquid hot water and AFEX pretreated distillers' grains at high-solids loadings. *Bioresource Technology* 99(12), 5206-5215 (2008).
81. Bobleter O: Hydrothermal degradation of polymers derived from plants. *Progress in Polymer Science* 19(5), 797-841 (1994).
82. Rinaldi R, Palkovits R, Schüth F: Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids. *Angewandte Chemie* 120(42), 8167-8170 (2008).
83. Rinaldi R, Meine N, Vom Stein J, Palkovits R, Schüth F: Which Controls the Depolymerization of Cellulose in Ionic Liquids: The Solid Acid Catalyst or Cellulose? *ChemSusChem* 3(2), 266-276 (2010).
84. Huber GW, Shabaker JW, Dumesic JA: Raney Ni-Sn Catalyst for H₂ Production from Biomass-Derived Hydrocarbons. *Science* 300(5628), 2075-2077 (2003).
85. Davda RR, Shabaker JW, Huber GW, Cortright RD, Dumesic JA: Aqueous-phase reforming of ethylene glycol on silica-supported metal catalysts. *Applied Catalysis B: Environmental* 43(1), 13-26 (2003).
86. Shabaker JW, Davda RR, Huber GW, Cortright RD, Dumesic JA: Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. *Journal of Catalysis* 215(2), 344-352 (2003).
87. Shabaker JW, Huber GW, Dumesic JA: Aqueous-phase reforming of oxygenated hydrocarbons over Sn-modified Ni catalysts. *Journal of Catalysis* 222(1), 180-191 (2004).
88. Oasmaa A, Czernik S: Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art for the End Users. *Energy Fuels* 13(4), 914-921 (1999).

Chapter 3. Steam Reforming of Bio-oil Fractions: Effect of Composition and Stability

A paper to be submitted to *Energy and Fuels* journal

Pedro J. Ortiz-Toral¹, Justinus Satrio³, Robert C. Brown^{2,3}, and Brent H. Shanks^{1,4}

Abstract

The efficacy of steam reforming of the aqueous species in bio-oils produced from the fast pyrolysis of biomass is examined. A fractionating condenser system was used to collect a set of fractions of fast pyrolysis liquids with different chemical characteristics. The water-soluble components from the different fractions were steam reformed using a nickel-based commercial catalyst in a fixed bed reactor system. When reforming at 500°C, an overall positive effect in hydrogen yields was observed for the fractions with higher concentrations of lower molecular weight oxygenates like acetic acid and acetol while the heavier compounds such as the carbohydrates showed an opposite effect. In general, higher selectivity towards hydrogen correlated to a lower tendency towards carbon deposits. Overall, the bio-oil fraction corresponding to the light end performed the best with the highest activity towards hydrogen. Carbon accumulation in the reactor was clearly a main issue during steam reforming of all of the bio-oil fractions studied. Chemical changes caused by aging of aqueous bio-oil were found to have a detrimental effect in hydrogen production.

Introduction

Chemically complex bio-oils from biomass fast pyrolysis can be captured in a fractionated collection system, which creates fractions with different chemical composition. Given these

¹Department of Chemical and Biological Engineering,

²Department of Mechanical Engineering,

³Center for Sustainable Environmental Technologies; Iowa State University, Ames IA, USA

⁴Author for correspondence: bshanks@iastate.edu

differing compositions there is the opportunity to utilize each fraction for different purposes. In particular, hydrogen might be a preferred product from a fraction that was rich in chemical species resulting from pyrolysis of the carbohydrate portion of biomass. Hydrogen is an important product as it will be required for upgrading of bio-oils to useable fuels. The relative ease by which individual bio-oils species or families of bio-oil species can be converted to hydrogen has not been determined as previous efforts on hydrogen production for bio-oil have focused on the entire bio-oil or the hydrophilic bio-oil species in total. Complicating this work is the fact that bio-oil stability issues impact the homogeneity and processability of these liquids.

The water insoluble portion of bio-oil is typically considered a high-value product due to its higher energy content than that of bio-oil as a whole.[1,2] It has been reported that this portion of bio-oil, which has commonly been referred to as pyrolytic lignin, could be converted to suitable fuels through processes such as hydrotreating.[3-8] However, hydrogen is required in significant quantity for this upgrading to biofuels via processes such as hydrodeoxygenation or hydrocracking. In a stand-alone fast pyrolysis-based biorefinery, the remaining bio-oil fraction (i.e. aqueous portion) derived mostly from the carbohydrate could in principle be steam reformed to generate more than enough hydrogen to supply the needs of any of these processes.[9]

Steam reforming (SR) of bio-oil compounds representing both the aqueous phase and the water insoluble phase have been tested mostly over Ni based catalysts.[10-14] Whole bio-oil or its water extractives have also been studied in the past.[13] While maximizing hydrogen production is the primary goal for these SR studies, catalyst stability has been reported to be a major issue limiting times on stream to around 5 hr in some cases even at low space velocities.[15] Carbon deposition has been identified as the primary cause for catalyst deactivation, which leads to compromised hydrogen yields. This effect is even more problematic when reforming whole bio-oils. The formation of carbon deposits is complex as it may arise from a combination of cracking, dehydration, and polymerization reactions. Ni as well as noble metal based catalysts have been tested in fixed bed and fluid bed reactors at elevated temperatures (700-900 °C) and steam to carbon (S/C) molar ratios (between 6-11) to

try to mitigate this issue.[13,16-19] Unfortunately, the chemical complexity of whole bio-oils does not readily allow for a systematic approach for determining how best to maximize hydrogen productivity while alleviating carbon deposition issues.

The development of a fast pyrolysis system with multi-fraction bio-oil collection capability presents an opportunity for studying fractionated bio-oils with different characteristics. Such a system, designed at Iowa State University, was equipped with a collection system as shown in Figure 4.[20] The bio-oil collection system allows bio-oil vapor and aerosols to be collected in up to five different fractions, each having unique physicochemical properties. In the current work, the bio-oil fractions were characterized and subjected to SR. The context of this work was focused on the production of hydrogen from the water-soluble portion of the bio-oil after the water insoluble fraction was separated. By having fractionated bio-oil samples, there is an opportunity to improve understanding of the complex SR characteristics of the water-soluble pyrolysis products. The SR results will be discussed in light of the chemical speciation of each of the bio-oil fractions.

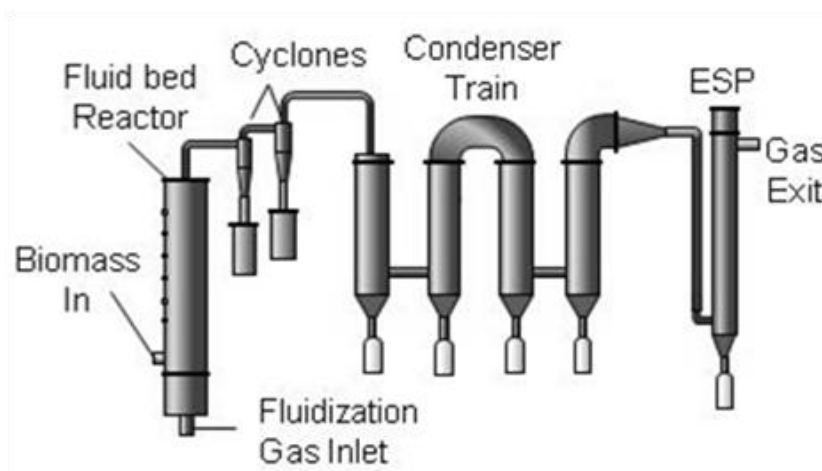


Figure 4. Schematic diagram of the fast pyrolysis reactor with staged bio-oil collection unit used to produce bio-oil (adapted from Ref [20])

Experimental Section

Generation of Bio-oil Fractions

The fast pyrolysis reactor used, for generating the bio-oil fractions, was an 8 kg/hr fluidized bed reactor as described previously Daugaard et al.[20, 21] The reactor exit was equipped with two cyclones connected in series to separate the char solids generated during pyrolysis from the vapor-gas stream. The bio-oil vapor-gas stream leaving the cyclones was immediately cooled and collected in five consecutive stages with the final stage being an electrostatic precipitator (ESP) that was used for capturing the aerosols produced including heavy water-insoluble compounds derived mostly from lignin. The bio-oil from the first fraction was excluded from this study as it was deemed unsuitable for SR since it contained only a small amount of water-soluble compounds and was solid at room temperature.

For this study the biomass source was cornstover, which in the United States is produced in large quantities typically in the Midwestern states. Prior to the pyrolysis reaction the biomass was dried to less than 11 wt% moisture and ground to 0.32 cm particle diameter using a hammer mill type grinder. The fluid bed reactor was operated at a bed temperature of about 520°C and atmospheric pressure. The fast pyrolysis resulted in 44 wt% bio-oil, 25 wt% char, 12 wt% gas of the mass balance. The unaccounted 19 wt% was mainly attributed to condensation and deposits on the reactor and line surfaces other than the condensers. The different bio-oil fractions had distinct tones of color and consistency.

A bio-oil from fast pyrolysis of cellulose was also included in this work as a levoglucosan-rich bio-oil (LRB). The cellulose bio-oil was collected as a single fraction composite for this study. Immediately after collection (within one hour), all corresponding bio-oil samples were capped and refrigerated to slow down the aging process, which would potentially change their properties with time.

Bio-oil Fraction Characterization

The four bio-oil fractions used as the basis for the SR study contained different levels of moisture and water insoluble materials and different chemical compositions. The physicochemical analysis methods used to characterize the fractions were based on the protocols described in detail by Oasmaa et al.[22] The elemental composition was determined by CHNS analysis based on gaseous product analysis. The water content was determined by Karl Fisher titration as per ASTM E203-96. The quantity of insolubles was determined by mixing bio-oil in water at a mass ratio of 1:80 to completely precipitate the insoluble material. The liquid was decanted and filtered. The remaining portion in the filter and flask gave the water insoluble content. The ash content was determined by weighing the residue after drying, combusting (at 775°C), and cooling about 20mL of each bio-oil fraction. The solids were defined by the portion that can be separated by filtration after thoroughly mixing the bio-oil in methanol at a ratio of about 1:20, while the high-heating values (HHV) were determined by bomb calorimetry.

Table 2. Characterization of the four whole bio-oil fractions

	Cond. 2	Cond. 3	Cond. 4	ESP
C, wt %	30.4	29.6	19.8	49.5
H, wt %	7.84	8.48	8.98	7.34
N, wt %	0.48	0.42	0.24	0.88
Ash, wt %	0.50	0.89	0.19	0.22
O by difference, wt %	60.8	60.7	70.8	42.1
Water, wt %	38.3	42.0	58.6	18.1
Water insoluble, wt %	9.46	3.63	0.61	27.0
Solids, wt %	3.42	4.46	0.18	1.43
HHV (MJ/kg)	13.6	14.5	10.9	24.6
pH	3.00	3.31	2.93	2.94
S/C _{whole} (mol/mol)	0.84	0.95	1.98	0.24
Water in aqueous extract, wt%	86.5	87.9	84.6	92.3

Aqueous Extraction of Bio-oil

Before performing the water extraction, the entire bio-oil fraction was homogenized in a sonicator bath for about 10 min. Then a representative sample of the homogenized bio-oil was subjected to the water-extraction step. The water addition to the bio-oil serves two purposes, to perform the extraction of the water-soluble species and also to adjust S/C ratio of the sample for its use as a reforming feedstock. The S/C fed to the reactor is defined as:

$$S/C = \frac{\text{moles of H}_2\text{O fed to the reactor}}{\text{moles of C fed to the reactor}} \quad (\text{Eqn. 7})$$

Achieving good control of the resulting S/C ratio of the aqueous extract was not simple as it depends on the amount of material that precipitates. This amount was found to not necessarily be linear with the amount of water used. Therefore the S/C ratio was adjusted based on the assumption that the material would stay in a single phase (S/C_{whole}) as follows:

$$S/C_{\text{whole}} = \frac{\text{moles of H}_2\text{O in the bio-oil fraction} + \text{H}_2\text{O added}}{\text{moles of C in the bio-oil fraction}} \quad (\text{Eqn. 8})$$

where the amount of water to be added was determined from the elemental analysis and moisture content of the bio-oil fraction by Eqn. 9.

$$\text{water}_{\text{add}} (\text{g/g}_{\text{bio-oil}}) = [(\text{desired } S/C_{\text{whole}})(\text{mol C}^a) - \text{mol H}_2\text{O}^a] * \text{MW}_{\text{H}_2\text{O}} \quad (\text{Eqn. 9})$$

^a per gram of bio-oil from corresponding fraction

The corresponding amounts of water added were: 3.26, 3.13, 1.79, and 5.75 g water/g bio-oil; for the fractions from condenser 2, 3, 4 and ESP, respectively. This approach also ensured that the bio-oil fractions with lower moisture content were separated using a larger amount of water to improve the phase separation.[23]

After the addition of the water the samples were mixed intensely and resonicated. The samples were then centrifuged and filtered to completely remove the precipitates. Then the aqueous samples were tested for moisture content after the procedure to determine the composition of each sample (see Table 2).

Steam reforming tests

The commercial reforming catalyst used was Reformax 330 LDP (11% Ni supported on alumina) as purchased from Süd Chemie. The catalyst rings were crushed and sieved to particles with diameter of 250-500 μm . The particles were packed into a quartz fixed bed flow reactor in a physical mixture with inert silicon carbide material to improve transport characteristics within the bed. The catalyst particle size was small relative to the reactor inner diameter (12.7 mm) but large enough to minimize pressure drop.[18] The catalyst was reduced in situ by introducing a 50/50 mixture of H_2 and N_2 at a total flow rate close to 200 mL/min at 550°C for 4 hr. The results reflect average values from steady state production of H_2 . The average time-on-stream was around 120 min.

A schematic of the reformer system is shown in Figure 5. The quartz reactor tube was 42 cm in length with a 12.7 mm of internal diameter and was held inside a temperature controlled electric furnace. A K-type thermocouple was located within the catalyst bed for controlling the overall reaction temperature. The catalyst bed was supported by a porous sintered quartz frit located above the vertical center of the reactor to minimize headspace pre-heating volume, which could promote cracking reactions of the feedstock prior to exposure to the catalyst bed. Due to the non-volatility of the water-soluble bio-oil, the feed was introduced in liquid form.

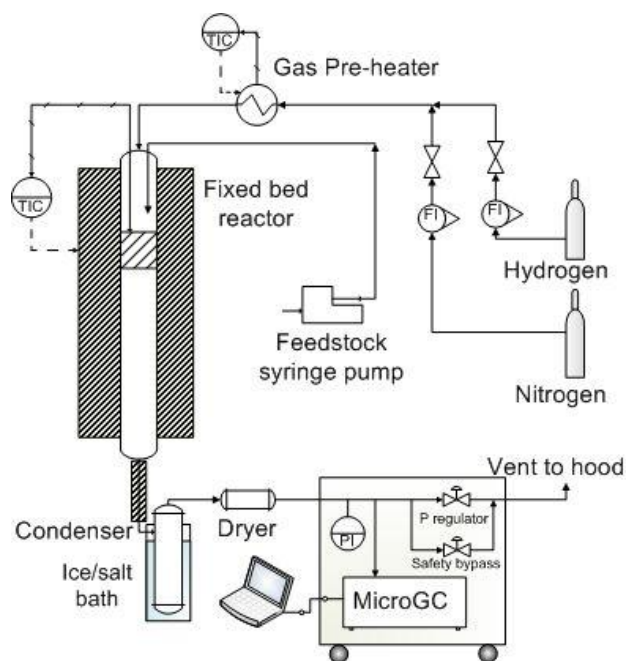


Figure 5. Schematic diagram of the steam reforming system

The liquid was introduced using a syringe pump (KD Scientific) through a capillary tube inside the reactor such that the liquid was injected about 3 cm above the hot catalyst bed surface. The liquid flow rate was set at 4.0 mL/hr. The corresponding WHSV was 0.87 hr^{-1} for all reaction tests. Nitrogen was introduced as a carrier gas and an internal standard through the top of the reactor. An ice/salt cooled impinger was used to condense the excess water and any condensable vapors present at the reactor exit. An in-line MicroGC (Varian CP-4900) system was used to analyze for the N_2 , H_2 , CO_2 , CO , CH_4 , and $\text{C}_2\text{-C}_3$ species in the effluent gas approximately every 3 min. The gas phase concentrations were determined by using calibration curves from standard gas mixtures. A bubble meter was used to monitor the effluent flow rate.

The hydrogen yield by weight of bio-oil species was calculated using Eqn. 10, in which the mass of hydrogen produced at steady state was determined relative to the total mass of the bio-oil compounds (dry basis) in the feed. The conversion to carbon gas species CO , CO_2 , CH_4 , C_2 , etc., was determined (Eqn. 11). This value can be used to estimate the amount of carbon accumulated in the reactor based on the carbon balance.

$$\text{H}_2 \text{ yield (wt\%)} = \frac{\text{mass H}_2 \text{ generated per min at S.S.}}{\text{mass of organics fed per min (dry basis)}} * 100 \quad (\text{Eqn. 10})$$

$$\text{C}_{\text{conv}} (\text{mol \%}) = \frac{\text{moles of C from product gases per min}}{\text{moles of feedstock C per min input}} * 100 \quad (\text{Eqn. 11})$$

The hydrogen yield relative to that possible by stoichiometry (Eqn. 12) was calculated for each of the fractions. These empirical formulas, which were based on elemental analysis, were determined on a dry basis. This approach addresses any differences in composition and degree of oxygenation of the species in the samples thereby providing a better basis for comparison. The maximum stoichiometric hydrogen was considered based on the complete reforming to H_2 and CO_2 .

$$\text{H}_2 \text{ stoich yield} = \frac{\text{moles H}_2 \text{ generated per min}}{\text{stoich max moles H}_2 \text{ per min}} * 100 \quad (\text{Eqn. 12})$$

Non-catalytic reforming

A series of reactor runs were performed over the inert packing material to quantify the extent of thermal reactions at different temperatures using a single S/C molar ratio. A bed of inert silicon carbide pellets was placed in the tubular reactor as the non-catalytic material. A single water-extracted portion of bio-oil was used for all of the “non-catalytic” tests. The overall testing procedure with the silicon carbide pellets followed a similar protocol to the catalytic tests.

Water addition effect

It has been reported in the literature that the SR of oxygenated species benefits from excess water conditions as it maximizes hydrogen production via the WGS reaction and gasification of carbon deposits.[24-26] The effect of water addition reported as S/C ratio was studied in

terms of hydrogen production. This also provided an opportunity to select a more targeted S/C for use in comparing the different fractions. A representative S/C_{whole} molar ratio was calculated for each bio-oil fraction. The fraction from condenser 4 was selected based on its minimal water insoluble content to eliminate any effect due to the quality of the phase separation. According to this, four solutions were prepared at different levels (S/C_{whole} of 4, 8, 12, and 18) and were subsequently steam reformed at 500°C.

Effect of bio-oil composition

Typically the SR reactions of the water-soluble portion of bio-oil or selected model compounds have been performed at temperatures between 550 and 800 °C [1,18,27], which are lower than those typically used with commercial natural gas reforming, which commonly lie between 800 and 870 °C.[28] This difference is due to the species contained in the water-soluble portion of bio-oil being more reactive than conventional feedstocks.[29] However, some research into bio-oil SR has been performed at conditions resembling those used for hydrocarbon steam reforming.[12,16,19] At the lower temperature range more typically used with bio-oil, both SR and water-gas shift (WGS) reactions can be performed simultaneously [26]. For this reason the different aqueous bio-oil fractions were subjected to SR at three different temperatures 500, 600 and 700 °C.

The bio-oil fractions used in the study came from condensers 2, 3, 4, and ESP as per the fractionated recovery schematic shown in Figure 4. In contrast, the bio-oil from cellulose pyrolysis resulted from recovery of the full bio-oil and not fractionated recovery. The fractions were characterized using a combination of GC-MS and GC-FID analysis to identify and quantify the major components and the SR results are presented as a function of the chemical composition of the different bio-oil fractions.

Bio-oil stability

Preliminary observations showed that the physical appearance of the aqueous bio-oil fraction samples changed upon storage. To determine how important these changes were on processing via SR additional tests were performed, which examined the SR performance of

aged samples. These results can help evaluate the storage potential of the hydrophilic fraction of bio-oil. An aqueous extracted bio-oil fraction was stored in tightly closed clear containers at room temperature away from direct sunlight. Aged samples of this solution were reformed after 30 and 90 days of storage. The impact of aqueous bio-oil aging was determined by evaluating the SR hydrogen yields and sample homogeneity of the stored samples.

Results and Discussion

Catalytic vs. Non-catalytic reactions

Catalytic and non-catalytic SR reactions of the aqueous extract from the condenser 2 fraction and with a S/C ratio of 8.9 were performed at 500, 600 and 700°C. Figures 6a,b show the product gas stream composition, H₂ yield, and carbon converted into the gas phase, respectively. As seen in Figure 6b, the catalytic reactions gave hydrogen as the main gas product followed by CO₂. The minimal presence of CO suggested high activity for the water gas shift reaction. A slight decrease in CO₂ with concomitant increase in CO was observed as the temperature increased. The non-catalytic reactions in which the reactor only contained silicon carbide resulted in an overall low production of gaseous products. At the higher reaction temperatures, CO was the primary gas product.

Figures 7a,b shows results for the calculated hydrogen yields with and without catalyst. In the absence of catalyst there was no significant conversion to hydrogen at any of the temperatures studied. Despite the lack of conversion to hydrogen, very little of the feed material was collected in the reforming reactor condenser suggesting nearly complete conversion towards carbon deposits. As the reaction temperature was increased, small amounts of hydrogen started to appear likely due to thermal decomposition or gasification reactions over the inert bed or reactor walls. The introduction of the catalyst into reaction system clearly shifted the conversion towards hydrogen. Within the temperature range studied, the temperature seemed to have a more pronounced effect on the non-catalytic reaction products than for the products resulting from the catalytic reactions.

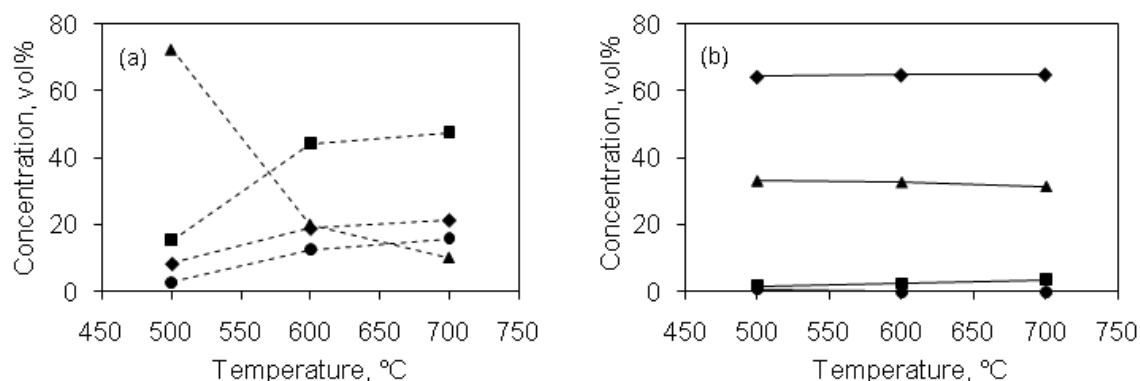


Figure 6. Steady-state gas composition plots of both catalytic and non-catalytic reactions (hydrogen ◆, carbon dioxide ▲, carbon monoxide ■, methane ●; plot (a) shows the non-catalytic products, plot (b) shows the catalytic products; concentrations in inert gas-free basis, lines added only as visual aids).

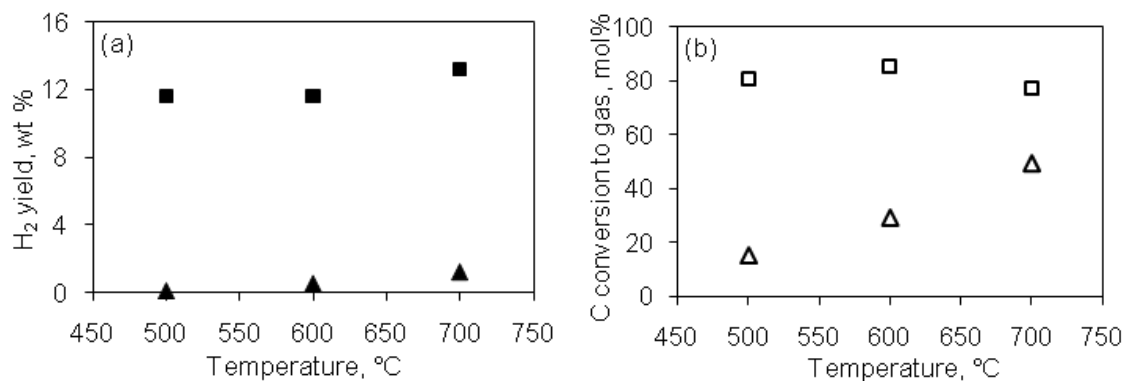


Figure 7. (a) Hydrogen yield comparison for non-catalytic (▲) and catalytic (■), (b) carbon conversion to gas products for catalytic runs (□) and non-catalytic (△) at different temperatures (aqueous condenser 2 fraction, S/C=8.9).

Figure 7b shows the total portion of carbon converted to gaseous products as a function of the reaction temperature with and without a catalyst. The distribution of the product gases was as described previously in Figure 6b. In the non-catalytic runs the carbon conversion approached 50 mol% as the temperature was increased to 700 °C with methane being the primary product. The data suggested that the conversion was primarily due to thermal decomposition and gasification reactions and not reforming. Comparison of these results with those from the catalytic runs suggested that at the higher temperatures the bio-oil fractions could readily react before coming into contact with the catalyst. Therefore, even when a

catalyst was introduced, a portion of the reaction could be controlled by thermal or non-catalytic reactions at higher temperatures. As such the catalytic reactions could proceed either directly through reforming of the bio-oil fraction or the conversion of intermediates generated from thermal decomposition. However, with the use of a reforming catalyst the overall reaction system shifted towards hydrogen and carbon dioxide production.

Effect of Water Addition

The effect of water addition on the yield of hydrogen from SR of the bio-oil fraction from condenser 4 at 500°C is shown in Figure 8. At S/C_{whole} molar ratios of 8, 12, and 18 the hydrogen yield was essentially equal, while the lower S/C_{whole} of 4 resulted in a reduced hydrogen yield. The results suggested that somewhere between S/C ratios of 4 and 8 a point was reached in which the addition of more water did not increase the yield of hydrogen in the gas product stream. The GCMS analysis on the condensables from the reactor exit stream showed no detectable bio-oil components, which indicated that the conversion of all the bio-oil components were essentially complete.

The results from the varying the S/C_{whole} ratio show at the lowest value there was limitation due to a combination of decreased WGS activity and higher overall rate of carbon accumulation. These reactions can be sensitive to the amount of water vapor available on the catalyst surface. These low S/C_{whole} values represent low water addition where there is a possibility of having small amounts of water insoluble material that could promote carbon deposition. Carbon deposition results in lower hydrogen productivity.[26] S/C_{whole} ratios of 8 or higher represent the water addition levels desirable to later compare different fractions excluding effect of the water vapor.

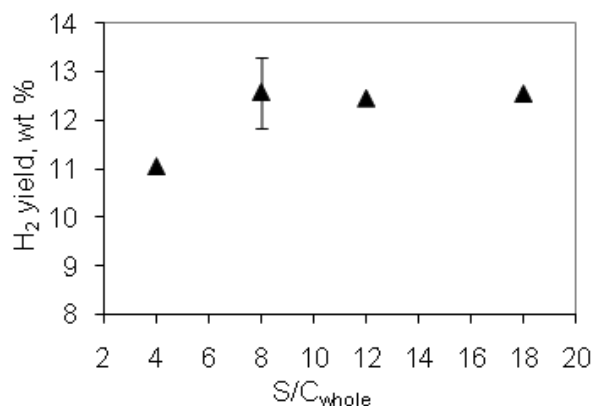


Figure 8. Hydrogen yield for different water addition levels at T=500°C (condenser 4 fraction, error bar represents the 95% confidence interval).

Effect of Sample Composition

The major compounds found in the aqueous extracted portions of the bio-oil fractions are presented in Table 4. Listed is the weight percent of the water and total organics in the samples. The species that make up the total organics are also shown with their weight percents listed. These values are given on their dry basis, e.g., if the water was not present.

Table 3. Composition of the different aqueous bio-oil extracts (wt%, wt% dry basis for the organic species).

	MW	Cond. 2	Cond. 3	Cond. 4	ESP	LRB
Water		86.7	87.6	84.5	91.6	86.3
Total organics		13.3	12.4	15.5	8.4	13.7
Acetic acid	60	21.7	18.4	45.5	2.1	30.7
Acetol	74	14.6	11.0	22.3	2.8	7.4
Furfural	96	19.8	5.09	5.98	7.27	0.45
5-methyl furfural	110	0.54	0.35	0.62	1.02	0.00
Levogluconan	162	23.4	9.6	16.7	29.3	60.7
Other		20.1	55.6	8.9	57.5	0.76

As clearly seen, there were different distributions of the compounds in the different fractions, but all of the fractions contained at least some amount of all the primary species. Therefore, the fractional condensation did modify the species distribution, but did not provide complete separation between the product species.

Acetic acid appeared to be enriched on condenser 4 fraction while in minimal amount on the ESP. The second low molecular weight species detected was acetol (hydroxyacetone). Acetol followed a similar concentration profile to that of acetic acid. Furfural was more prominent in condenser 2. Another substituted furan, 5-methyl furfural, was detected more prominently at the ESP fraction although at very low level. Levoglucosan (1-6-anhydro- β -D glucopyranose), which is an anhydrosugar that is a major product from cellulose pyrolysis [30], was found at its highest concentration in the ESP followed by condenser 2, condenser 4, and in condenser 3. The balance of the organic species, listed as others, corresponded to trace compounds and species not detectable by gas chromatography (non volatile).

Overall, the samples from the ESP and condenser 2 were found to contain increased content of the higher molecular weight species. In contrast, lower molecular weights species were more prevalent in condensers 3 and 4. The LRB sample, which was obtained from collecting all of the liquid products from pure cellulose pyrolysis, was found to consist primarily of levoglucosan (61%), acetic acid (31%), and acetol (7%).

Figure 6 shows the plots of hydrogen yields from reforming of aqueous portions from the fractions as function of reaction temperature. Replicate SR tests were performed at 500 °C to determine standard deviation as a measurement of experimental error (as shown in Figure 9). Based on this analysis, no overall difference in hydrogen yields were observed for a given fraction across the three different temperatures. For the different fractions the hydrogen yields appeared to also be quite similar; however, there were a few key differences. The ESP fraction gave depressed hydrogen yield relative to the other fractions and the LRB sample, which was only reformed at 500°C, resulted in a lower hydrogen yield than any of the condenser fractions.

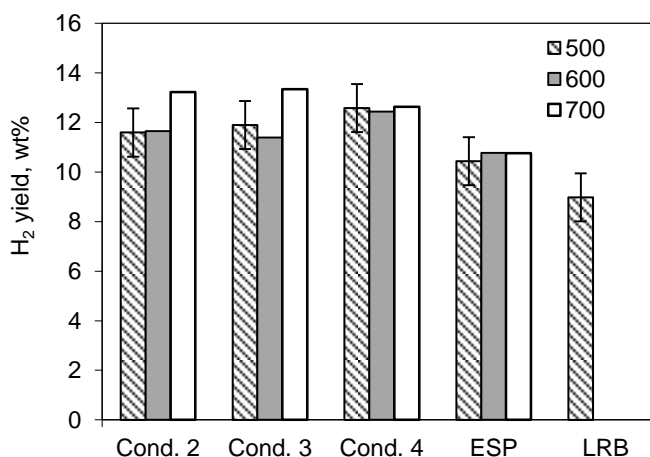


Figure 9. Hydrogen yield based on the amount fed (wt. dry basis) of the different samples at three different reaction temperatures.

GC analysis of the liquid condensate collected from the reactor outlet stream indicated that there were no detectable amounts of unreacted organic compounds in any of the catalytic runs, so the samples were effectively converted completely across the reactor. Presented in Figure 7a is that overall carbon conversion, which gives the amount of carbon present in the feed to the reactor that was converted to gaseous species. As no unreacted species were found in the post-reforming reactor condenser, any carbon that was not converted to gas phase species was deposited as carbon within the reactor. Therefore, the amount of accumulated carbon within the reactor for each of the runs was calculated with the results shown in Figure 7b. With the exception of the reactions at 500°C, it can be seen that the amount of carbon converted to gas products were in general not significantly affected by differences in sample compositions.

The carbon, which accumulated inside the reactor, was either on the reactor surfaces or the catalyst surfaces. After completion of each of the reforming reaction experiments, carbon deposition was observed (could be seen through the walls of the quartz reactor tube). Given the significant amount of carbon accumulation in the reactor, finding a steady state hydrogen production phase was difficult for some of the reaction conditions. This issue was more pronounced during SR reaction tests for temperatures above 600°C.

As shown by the calculated result in Figure 10b, the apparent carbon deposition at 500 °C was lower for the condenser 4 fraction than with the ESP and LRB, which was confirmed by visual inspection of the reactor after the respective experiments.

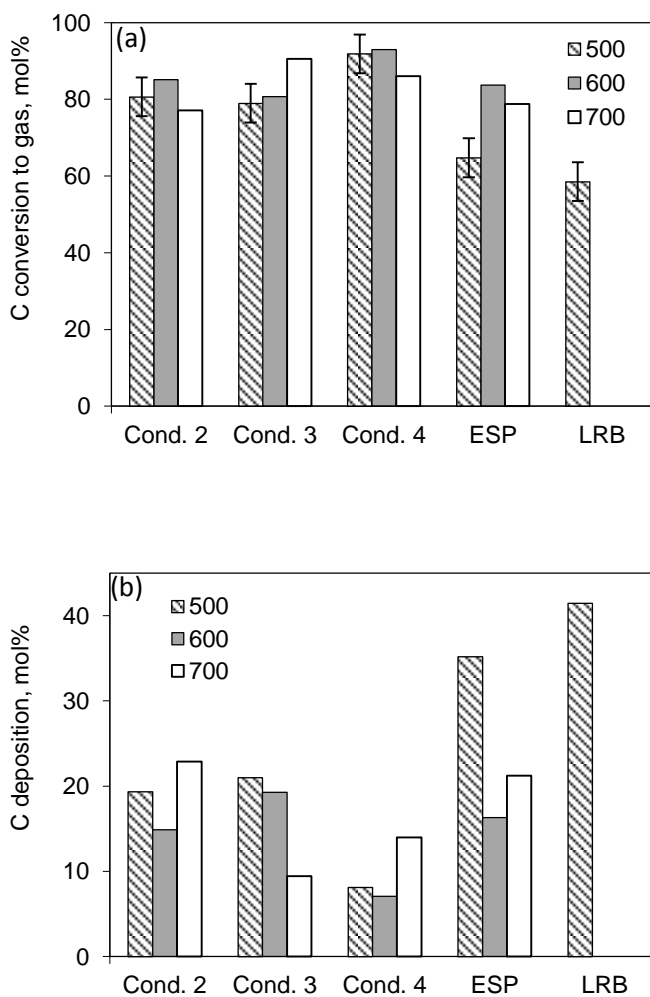


Figure 10. (a) Carbon conversion to gas products; (b) Estimated fraction of carbon deposited from the different samples.

The LRB sample was the most discrepant as it gave the lowest amount of gaseous carbon products, which corresponded to a higher level of carbon deposition. For this run, in particular, a large quantity of carbon deposits was visible in the top region of the catalyst bed at the end of the experiment.

This observation suggested that levoglucosan was particularly prone for creating carbon deposition, which occurred as soon as it was exposed to the catalyst bed. As shown previously, carbon deposition creates a significant limitation on the time on stream as well as on the hydrogen yields.[1,10,11,17-19,26,27,31] These carbon deposits can limit the SR reaction both through deactivating the catalyst or physically blocking the flow of reactants through the reactor.[16,25,32-35]

Figure 11 shows the stoichiometric hydrogen yields of the reforming reactions from the different fractions (calculated using Eqn. 12), compared with values that have been reported in the literature. These values represent hydrogen production corresponding to complete conversions of the bio-oil samples.

The elemental analysis results used to determine the maximum possible stoichiometric yields in the hydrogen yield calculations are given in Table 4. It is interesting to note that despite the differences in species composition of the samples, the samples had very similar C, H, and O concentrations. The SR experiments showed no significant difference between the hydrogen yield from condenser 2 and condenser 3 samples (Figure 11). These values were comparable with published data for water-soluble bio-oil SR under similar conditions.

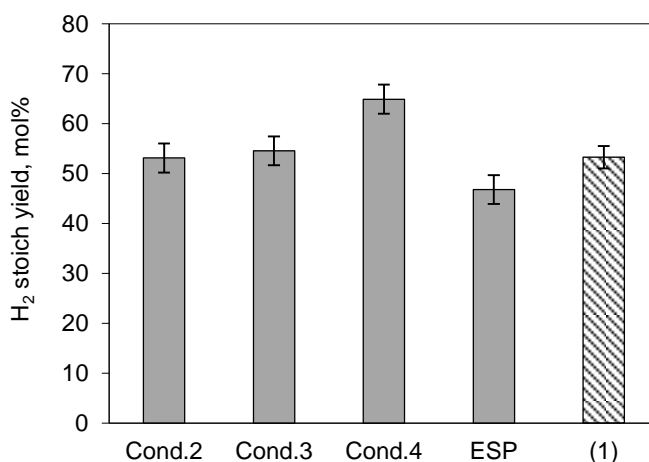


Figure 11. H₂ stoichiometric yield of four of the samples reformed at T=500°C; (1) Kechagiopoulos et al. [18] aqueous bio-oil tests T=600-700°C, S/C=8.2.

Table 4. Elemental analysis of the set of aqueous samples (wt% dry basis) and corresponding empirical formulas (per mole of carbon basis).

	Cond. 2	Cond. 3	Cond. 4	ESP
C	48.7	49.7	46.0	47.5
H	11.1	10.7	9.8	12.1
O	40.2	39.5	44.3	40.4
n (C)	1	1	1	1
m (H)	2.75	2.59	2.54	3.06
k (O)	0.62	0.6	0.72	0.64

However, there was a difference between the hydrogen yields of these samples and those obtained from the condenser 4 and ESP samples. The highest hydrogen yield was observed for condenser 4, which was the sample characterized by the largest presence of the two lightest compounds, i.e., acetic acid and acetol. There was also a notable reduction in hydrogen production resulting from SR the ESP sample. As shown previously in Table 3, the ESP fraction was composed mainly of heavier compounds, such as levoglucosan and phenolic compounds. This fraction would be anticipated to be more difficult to reform to hydrogen than the lower molecular weight species.

Using the experimental SR results for the fractions, a correlation between the concentrations of the key individual species within the samples with respect to the hydrogen yield was evaluated. Figure 12a,b shows the correlative effect of the concentration of the quantified compounds in each of the samples, i.e. acetic acid, acetol, furfural, levoglucosan, and 5-methyl-furfural, for SR at 500°C. It is important to note that the hydrogen yield is that corresponding to specific samples, which means that the effects of the individual components are convoluted. Nevertheless, correlative trends could still be observed for each of the primary species, which can serve as a building block for further study on the performance of individual bio-oil components during reforming reactions.

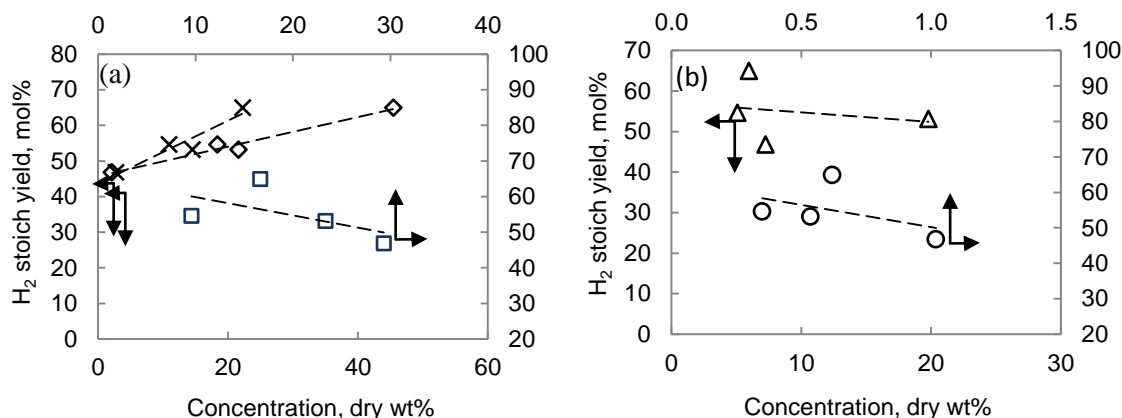


Figure 12. Effect of concentration for the most relevant species; (a) acetic acid (◇), acetol (X), and levoglucosan (□); (b) furfural (△), and 5-methylfurfural (O); arrows indicate the corresponding axes for each data set.

Figure 12a shows the effects of the concentration of acetic acid, acetol, and levoglucosan on the hydrogen yield. Both acetol and acetic acid concentrations showed a positive proportional effect of increased hydrogen yields with an increase in their concentrations. In contrast, levoglucosan appeared to be negatively correlated, i.e., lower hydrogen yield when its concentration increased. While not as strongly correlated as levoglucosan, furfural and 5-methylfurfural seemed to have a slightly negative correlation (Figure 12b). These results were consistent with those reported previously by Primm et al. in which higher molecular weights and levels of unsaturation led to diminished hydrogen production in hydrocarbon steam reforming [36].

Bio-Oil Stability

The appearance of the fresh aqueous bio-oil fraction samples was translucent red color and was clear of particulates. However, upon storing the samples became darker and cloudier. The extracted bio-oil fraction chosen for the stability study was allowed to age for a period of 90 days. After 30 days the extracted sample was found to have suspended dark particulate matter. During the aging process the samples were able to be re-homogenized using an ultrasound treatment, but the samples stored for a period of over 90 days were not able to be completely re-homogenized even by using this method. Chemical characterization of the

aged solutions showed a decrease in the acetic acid, acetol and levoglucosan concentrations (data not shown). It has been proposed previously that the aging of these solutions involves polymerization reactions. The actual aging products were not successfully identified when methods that have been described earlier were used.[23,37] In general, one would anticipate that the polymerization products would negatively impact catalytic steam reforming as they would have higher molecular weight.

The hydrogen yields corresponding to steam reforming of the condenser 4 bio-oil fraction upon extraction and after aging for 30 and 90 days, respectively, are presented in Figure 13. A significant rapid diminishment in hydrogen production after only 30 days of aging was observed, which demonstrated that the chemical changes occurring during aging of the solution were detrimental for hydrogen production even for this lighter end fraction of bio-oil. At the endpoint of the stability study (90 days) further aging was observed in terms of solution turbidity and loss of the ability to re-homogenize solution. However, the hydrogen yield for this 90-day aging sample showed no further change in hydrogen productivity relative to sample aged for 30 days. From these tests it can be concluded that these aqueous bio-oil samples age quickly at room temperature producing a material that is more difficult to reform.

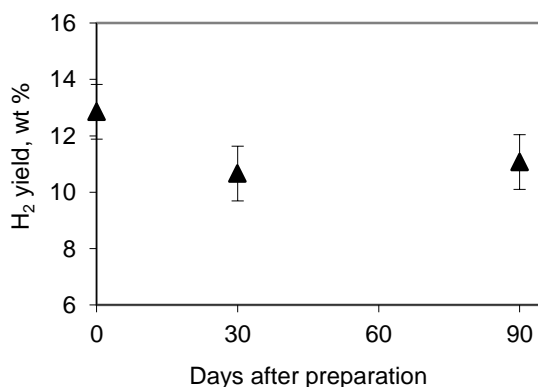


Figure 13. Effect of storage time after water addition on hydrogen yield.

A study was also performed on evaluating the effect of the presence of suspended material on the resulting reforming performance. The hydrogen production from steam reforming a

sample stored for more than 90 days was compared to that from the reforming of a sample from the same batch that had been filtered to remove the particulate material.

The filtered sample was mostly homogeneous with a dark amber color. As shown in Figure 14(a, b), the results from reforming of these two samples did not show any clear difference in the resulting hydrogen yield or carbon conversion. Therefore, the suspended material observed in the aged bio-oil does not appear to be the primary cause of the poorer reforming performance seen after very short aging times, which means the aging effect on reforming performance of the bio-oil fraction must rely primarily on chemical changes involving chemical species that are still in solution.

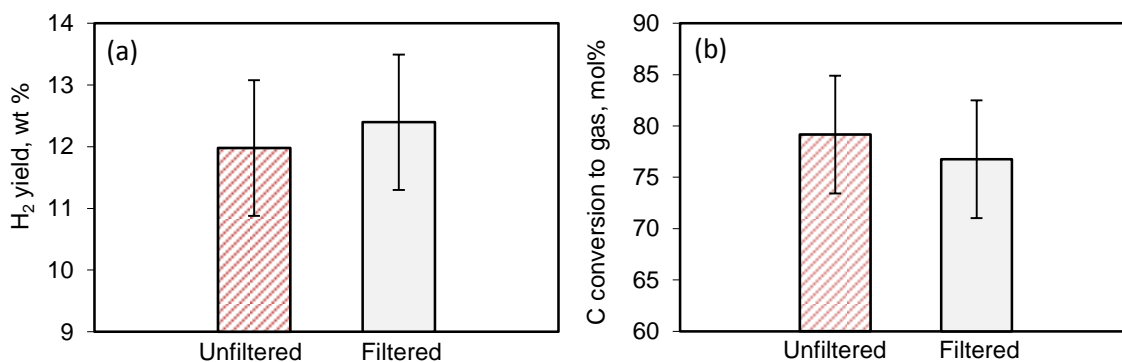


Figure 14. (a) Hydrogen yield of aged bio-oil solution before and after filtration, (b) carbon conversion before and after filtration.

Conclusions

Given their high oxygen content, biomass-derived bio-oils will not have the same hydrogen production characteristics via steam reforming relative to those for hydrocarbon feedstocks. As shown from the non-catalytic tests with aqueous bio-oil fractions at temperatures higher than 500°C, thermal decomposition reactions play a role in the reaction. This result suggests that when a catalyst is used for steam forming of bio-oil species that a combination of both thermal and catalytic conversion can occur. In the presence of a Ni catalyst, complete conversion of aqueous bio-oil species and readily occur at temperatures as low as 500°C. In

contrast to hydrocarbon reforming, which requires higher temperatures for reforming, the lower reforming temperature for bio-oil reforming will favor the water-gas shift (WGS) reaction, so higher amounts of carbon dioxide relative to carbon monoxide are found in the product. This effect diminished the need for a downstream WGS reactor to obtain maximum hydrogen yields. Water addition levels for the bio-oil species corresponding to S/C between values of 4 and 8 could be used without sacrificing the amount of hydrogen that could be produced.

The experimental results showed that the species present in a light-end bio-oil fraction were most suitable for efficient hydrogen production. Therefore, bio-oil fractions that were richer in low molecular weight species like acetic acid and acetol seemed to convert more effectively to hydrogen while the presence of heavier molecules like levoglucosan and furfural in other fractions had a detrimental impact on hydrogen production. While an overall relationship was observed between the molecular weight of the molecules reformed and their ease of reforming and extent of carbon deposition, these effects could not definitively deconvoluted due to the use of complex mixtures present in real bio-oil fraction samples.

Aqueous or water-soluble bio-oil samples were unstable leading to apparent change in chemical properties, which were difficult to quantify by chemical analysis. However, aging of the aqueous bio-oil fraction samples proved to be detrimental to hydrogen production via SR. Additional fundamental studies of model bio-oil species that also incorporate coke quantification methods would help to better elucidate the effects underlying the observations in this study. An improved understanding of the underlying steam reforming characteristics of the different chemical species present in bio-oils will provide the opportunity to predict hydrogen yields and to identify undesirable compounds.

Acknowledgment. This work was performed with the support of the U.S. Department of Agriculture, project number 68-3A75-5-233.

References

1. Galdamez JR, Garcia L, Bilbao R: Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni-Al Catalysts. Acetic Acid as a Model Compound. *Energy Fuels* 19(3), 1133-1142 (2005).
2. Czernik S, Bridgwater AV: Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy & Fuels* 18(2), 590-598 (2004).
3. Huber GW, Corma A: Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass. *Angewandte Chemie International Edition* (46), 7184-7201 (2007).
4. Bridgwater AV, Cottam M-L: Opportunities for Biomass Pyrolysis Production and Upgrading. *Energy & Fuels* 6(2), 113-120 (1991).
5. Elliott DC, Neuenschwander GG: In: *Developments in Thermochemical Biomass Conversion*, Bridgwater AV, Boocock, D. G. Blackie Academic and Professional, London (1996).
6. Shabtai JS, Zmierzak WW, Chornet E: *The University of Utah Research Foundation* US Patent 5959167, (1999).
7. Bridgwater AV: Catalysis in thermal biomass conversion. *Applied Catalysis A: General* 116(1-2), 5-47 (1994).
8. Furimsky E: Catalytic hydrodeoxygenation. *Applied Catalysis A: General* 199(2), 147-190 (2000).
9. Brown RC: The Role of Thermochemical Technologies in Advanced Biorefineries. At the North Central Region Feedstock Workshop. (August 2006).
10. Wang DN, Czernik S, Chornet E: Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. *Energy & Fuels* 12(1), 19-24 (1998).
11. Garcia L, French R, Czernik S, Chornet E: Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Applied Catalysis A: General* 201(2), 225-239 (2000).
12. Markevich M, Czernik S, Chornet E, Montane D: Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil. *Energy Fuels* 13(6), 1160-1166 (1999).
13. Czernik S, French R, Feik C, Chornet E: Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Industrial & Engineering Chemistry Research* 41(17), 4209-4215 (2002).
14. Wang Z, Pan Y, Dong T *et al.*: Production of hydrogen from catalytic steam reforming of bio-oil using C12A7-O--based catalysts. *Applied Catalysis A: General* 320, 24-34 (2007).
15. Li H, Xu Q, Xue H, Yan Y: Catalytic reforming of the aqueous phase derived from fast-pyrolysis of biomass. *Renewable Energy* 34(12), 2872-2877 (2009).
16. Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R: Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Applied Catalysis B: Environmental* 61(1-2), 130-139 (2005).
17. Basagiannis AC, Verykios XE: Steam reforming of the aqueous fraction of bio-oil over structured Ru/MgO/Al₂O₃ catalysts. *Catalysis Today* 127(1-4), 256-264 (2007).

18. Kechagiopoulos P.N., Voutetakis S., Lemonidou A., I AV: Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-oil in a Fixed Bed Reactor. *Energy and Fuels* (20), 2155-2163 (2006).
19. Czernik S, Evans R, French R: Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catalysis Today. Recent Advances in Catalytic Production of Hydrogen from Renewable Sources* 129(3-4), 265-268 (2007).
20. Daugaard DE: The transport phase of pyrolytic oil exiting a fast fluidized bed reactor. *Mechanical Engineering Doctor of Philosophy*, 139 (2003).
21. Daugaard DE, Brown RC: Enthalpy for Pyrolysis for Several Types of Biomass. *Energy Fuels* 17(4), 934-939 (2003).
22. Oasmaa A, Peacocke C: A Guide to Physical Property Characterization of Biomass-derived Fast Pyrolysis Liquids. *VTT Energy, Espoo, Finland*, 65. + App 34 (2001).
23. Boucher ME, Chaala A, Pakdel H, Roy C: Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase. *Biomass and Bioenergy* 19(5), 351-361 (2000).
24. Huber GW, Iborra S, Corma A: Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 106(9), 4044-4098 (2006).
25. Kechagiopoulos P., E. Vagia, A. Iordanidis, S. S. Voutetakis, A.A. Lemonidou, Vasalos IA: Hydrogen production from renewable energy sources: reforming of biogas and bio-oil. *Catalysis, Energy and Environment. Workshop of CPERI*, (2004).
26. Wang D, Montane D, Chornet E: Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde. *Applied Catalysis a-General* 143(2), 245-270 (1996).
27. Vagia EC, Lemonidou AA: Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts. *Applied Catalysis A: General* 351(1), 111-121 (2008).
28. Czuppon TA, Knez SA, Newsome DS: *Hydrogen*. In: *Encyclopedia of Chemical Technology*, Kroschwitz JI, Howe-Grant M. John Wiley & Sons, New York pp 852-859 (1995).
29. Evans RJ, Czernik S, Marda J: Distributed Bio-Oil Reforming. *DOE Hydrogen Program FY 2007 Annual Progress Report*, (2007).
30. Mohan D, Pittman CU, Steele PH: Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* 20(3), 848-889 (2006).
31. Takanabe K, Aika K-I, Seshan K, Lefferts L: Sustainable hydrogen from bio-oil-- Steam reforming of acetic acid as a model oxygenate. *Journal of Catalysis* 227(1), 101-108 (2004).
32. Iojoiu EE, Domine ME, Davidian T, Guilhaume N, Mirodatos C: Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia. *Applied Catalysis A: General* 323, 147-161 (2007).
33. Basagiannis AC, Verykios XE: Catalytic steam reforming of acetic acid for hydrogen production. *International Journal of Hydrogen Energy* 32(15), 3343-3355 (2007).

34. Takanabe K, Aika K-I, Inazu K, Baba T, Seshan K, Lefferts L: Steam reforming of acetic acid as a biomass derived oxygenate: Bifunctional pathway for hydrogen formation over Pt/ZrO₂ catalysts. *Journal of Catalysis* 243(2), 263-269 (2006).
35. Basagiannis AC, Verykios XE: Reforming reactions of acetic acid on nickel catalysts over a wide temperature range. *Applied Catalysis A: General* 308, 182-193 (2006).
36. Trimm DL: Coke formation and minimisation during steam reforming reactions. *Catalysis Today* 37(3), 233-238 (1997).
37. García-Pérez M, Chaala A, Roy C: Vacuum pyrolysis of sugarcane bagasse. *Journal of Analytical and Applied Pyrolysis* 65(2), 111-136 (2002).

Chapter 4. Steam Reforming of Bio-oil Model Compounds: Reactivity and Carbon Deposition Studies

A paper to be submitted to the Energy and Fuels Journal

Pedro J. Ortiz-Toral¹, Robert C. Brown^{2,3}, and Brent H. Shanks,^{1,4}

Abstract

It has been seen in the past how bio-oil fractions composed mainly of light species are more favorable to the production of hydrogen via steam reforming when compared to heavier fractions. Catalyst deactivation by coking and a high degree of thermal decomposition are the major known limitations although the responsible species have not yet been identified. Model compounds representing different types of functionalities and molecular weights in bio-oil were selected to determine relative reactivity and tendencies to generate solid carbon. Acetic acid, furfural, glycolaldehyde, levoglucosan and acetol were chosen to model carboxylic acids, aldehydes, anhydrosugars and other multi-functionalized oxygenates. These feedstocks were tested in a small fixed bed catalytic reactor in the presence of excess steam under kinetic control conditions. The order of decreasing reactivity in terms of conversion was levoglucosan > acetic acid > glycolaldehyde > acetol > furfural for the temperature range tested. The order of decreasing carbon deposition level was levoglucosan > acetic acid > furfural > glycolaldehyde > acetol. The levoglucosan showed highest carbon deposition from non-catalytic decomposition while acetic acid, furfural and acetone showed the highest extent of catalyst coking. The carboxylic acid was identified as the most abundant of the troublesome species. Results suggested that among the carboxylic acids there was a relationship between the coking tendency and the amount of C-C bonds to break.

¹Department of Chemical and Biological Engineering,

²Center for Sustainable Environmental Technologies,

³Department of Mechanical Engineering; Iowa State University, Ames, Iowa 50011

⁴Author for correspondence: bshanks@iastate.edu

Introduction

Two of the major concerns with the use of fast pyrolysis bio-oil as a biofuel are its high oxygen and water content.[1] Hydrogen required for upgrading these biofuels can be generated from steam reforming specific fractions of the bio-oil. Bio-oil can be separated into a water insoluble portion and water-soluble portion.[2] In the case of bio-oil from forestry residue about 15-20 wt% has been identified as water insoluble material, 25-30 wt% water and roughly 48-60 wt% as water-soluble oxygenates.[3] The water insoluble portion could be catalytically upgraded to hydrocarbons while the water-soluble portion can be steam reformed to generate the hydrogen.[4,5]

The steam reforming of water-soluble bio-oil is quite complex as it is generally considered non-volatile and prone to carbon deposition.[6] In laboratory reactors the bio-oil needs to be introduced as a liquid. During feeding the thermally unstable liquid is exposed to hot reactor walls that become reactive.[7-10] The thermal instability arises from the bio-oil complexity but may be related to key species or types of species.[6] Ideally, the feed mixture should vaporize only upon contact with the catalytic bed to avoid carbonization on reactor surfaces. As the vapor passes through the bed and gases are generated, carbon deposits accumulate on top of and within the bed. It is very important that these issues are taken into account further studies of the fundamentals of bio-oil steam reforming.

The nature of the specific reactions that limit the efficiency in hydrogen production is not well understood. Some of these issues have been addressed in the past using different approaches with limited success. One of these approaches included the investigation of process conditions to maximize hydrogen production by promoting gasification of carbon deposits with elevated temperatures and high S/C (steam to carbon) ratios using single model compounds.[11-14] Another interesting approach has been the catalyst screening employing either a model compound or full bio-oil. Fluidizable catalysts have also been investigated which would shear off the carbon deposited and thus increase the catalyst stability.[8,15-18] In this type of system the challenge then lies on improving the mechanical and shear strength

of the materials. It is important to remember that the carbon formed compromises the hydrogen yields nevertheless.

As mentioned before, one of the main challenges with bio-oil or water-soluble bio-oil steam reforming lies with its chemical complexity. In the past different bio-oil fractions were tested where the aqueous portions of light fractions proved to be better for hydrogen production. The fraction containing mostly low molecular weight water-soluble oxygenates showed the highest hydrogen yields at the expense of carbon deposition. In many cases, severe carbon deposition was observed in some instances leading to quick reactor plugging. It is clear that there are certain challenges in completely deconvoluting the effects of bio-oil chemical composition due to the complexity of bio-oil and even bio-oil fractions. Thus it becomes important to study in more depth the carbon deposition tendencies from individual bio-oil species. A key step of this approach is to identify and gain some insight into the problem species within the water-soluble bio-oil.

The relative reactivity of representative water-soluble bio-oil model species as well as their carbon formation tendency becomes important in order to better understand their underlying characteristics. For this study the species contained a range of molecular weights and different functionalities (Table 5). Acetic acid, furfural (furfuraldehyde), glycolaldehyde (2-hydroxyacetaldehyde), levoglucosan (1,6-Anhydro-*beta*-glucopyranose) and acetol (1-hydroxyacetone) were chosen to model water-soluble carboxylic acids, aldehydes, furans, anhydrosugars, and other multi-functionalized oxygenates. These molecules have been identified as some of the most abundant in water-soluble bio-oil (See Chapter 3). It is important that the troublesome species or types of species are identified.

It can be observed, for example, that acetic acid and glycolaldehyde have the same elemental make-up and molecular weight, thus their difference lies on the molecular arrangement of functional groups. Some of these species are multifunctional like furfural and glycolaldehyde while having aldehyde moieties in common.

Table 5. Model compounds and stoichiometry of steam reforming to H₂ and CO₂

Compound	MW	Reactants ^a			Products ^a		
		n (C) ^b	m (H) ^b	k (O) ^b	H ₂ O (2n-k)	CO ₂ (n)	H ₂ (2n+m/2-k)
Acetic acid	60	2	4	2	2	2	4
Glycolaldehyde	60	2	4	2	2	2	4
Acetol	74	3	6	2	4	3	7
Furfural	96	5	4	2	8	5	10
Levoglucosan	162	6	10	5	7	6	12

^a in mol/mol of reacted species

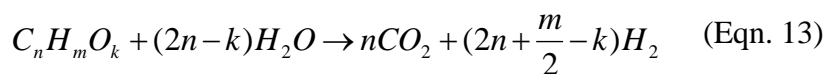
^b n,m and k come from chemical formula subscripts

Acetol contains an additional carbon when compared to glycolaldehyde, making it a ketone but also an alcohol. Furfural and levoglucosan have ring structures of different carbon numbers. Furfural although abundant in typical bio-oil is only partially water-soluble so it's abundance in aqueous extracted bio-oil can be very limited.

Even though glucose and sucrose are commonly used to model the carbohydrates in bio-oils, in reality anhydrosugars like levoglucosan are the most abundant carbohydrates found in typical bio-oils.[19,20][21,22] The fact that significant amounts of levoglucosan can be recovered from the pyrolysis vapors suggests this molecule may have unique thermal properties when compared to other carbohydrates. For this reason it is important to consider the behavior of this molecule to better describe the steam reforming of bio-oil mixtures.

The stoichiometry of the steam reforming (Eqn. 13) of the model compounds is presented in table 1. The table includes the species molecular weights and the carbon chain length (C_n , where n is the chemical subscript) as reference. The water requirement for complete steam reforming and stoichiometric potential for H₂ and CO₂ are also presented.

Steam reforming of oxygenated hydrocarbons:



For this study the reactions were studied in a kinetically controlled set of conditions to better describe the species interaction with the reforming catalyst while minimizing the effect of

thermodynamic equilibrium or transport phenomena. These results can then be used to describe intrinsic properties like reactivity and tendency towards carbon deposition of the model species. Future work may then focus on the issues related to the troublesome species or functionalities found as found on this work.

Experimental

Reactor setup

Steam reforming experiments were performed using a tubular fixed bed reactor setup elsewhere described in more detail (See Chapter 4). There were a series of modifications for operating at lower conversions while minimizing transport limitations. The quartz reactor had an internal diameter of 0.64 cm and a total reactor length of 46 cm. A thermocouple was placed inside the bed to measure a representative catalyst temperature.

The liquid feed flow rate was set at 6.0 mL/hr providing a drop over the bed surface approximately every 8 s. Nitrogen gas was fed as sweep gas and internal standard at 60.0 mL/min. The liquid feed was injected no more than 4 cm above the top of the catalyst bed using a 0.8 mm inner diameter capillary tube with a diagonal cut at the tip. For the length of the injector the reactor was shielded with ceramic wool to prevent direct radiation from the furnace to prevent plugging by carbon deposits. The intent of this was to provide quick contact of the feedstock and the catalyst while minimizing preheating.

The catalyst was packed on top of a quartz wool plug and supported by a quartz frit located near the vertical center of the reactor. The amount of catalyst was varied between 25 and 75 mg. The bed was packed together with inert SiC material to improve heat and transport properties. The catalyst used was a commercial Ni/Alumina reforming catalyst, Reformax 330DP from Sud Chemie (11 % Ni loading), ground and sieved to different sizes from under 106 up to 1000 μm . Fresh catalyst was used for each reaction to eliminate the effect of catalyst stability. The catalyst was reduced before each reaction at 550°C for 4 hr with a 50/50 flow of H_2 and N_2 .

The top and bottom sections of the reactor were heated by heat tapes set at 140 °C to prevent condensation. The reactor effluent contained product gases, the unreacted portion of the feedstock, and any condensable by-products. Condensates were collected into two condensers in a salt-ice bath. Methanol or acetone was used as bubbling media to improve the efficiency of the catch. Any moisture left in the gas stream was removed by flowing through Drierite material. A slipstream of the effluent was analyzed by in-line GC (described later). The total flow rate of the effluent stream was measured continuously using a volumetric bubble flow meter that was connected to a vent. Standard reaction time was 80 min, which is around the time the reactor plugged during some preliminary experiments.

Sample preparation

The model chemicals used were obtained as reagent grade, when available, from Sigma Aldrich. These model species were premixed with DI water to achieve a S/C of 6 for the base cases with the exception of furfural (S/C=19) due to its low solubility in pure water. This insured that the water vapor was in excess so that the reactions were limited by the reactivity of the reformed species. The reaction temperatures were held between 420 and 460°C, to slow down the reactions while avoiding the gasification of carbon deposits, under atmospheric pressure. At these reaction conditions both the steam reforming reactions and the water-gas shift reactions are to happen in a single operation. Note that the water-gas shift reaction is favorable thermodynamically at these conditions while the steam reforming to H₂ and CO is usually performed at elevated temperatures.

Analytical methods

A sample of the gas stream exiting the reactor was analyzed approximately every 3-4 minutes with a Varian CP-4900 MicroGC. The evolution and steady-state in concentrations of H₂, CO₂, CO, CH₄ gases were determined by calibration curves from gas standards. The water-rich condensate samples were analyzed by a GC (Varian 430-GC) equipped with a 30 m long Restek Stabilwax column and an FID detector. For the analysis of levoglucosan samples, a short 15 m semi-polar Varian VF1 column was used instead. The overall conversion of the

feedstock for each reaction was determined from the analysis of the unreacted portion found in the condensates.

In situ temperature programmed oxidation with air (Air-TPO) method was performed to quantify the carbon deposits from steam reforming. This method was favored since elemental analysis (CHN) of the recovered catalyst led to incomplete mass balances for some species. An in-situ method would clearly account for all carbon accumulated including that portion contained on the reactor surfaces. This method also provides the opportunity to obtain some characterization information on the carbon deposits.

After each reforming reaction the reactor was cooled down to approximately 110°C while being purged with N₂ flow. The reactor was held at this temperature for about 15 min or however long necessary to remove moisture and carbon species like CO₂ from the system. For the TPO the temperature was ramped from room temperature to 720°C at a rate of 8 °C/min under flow of air at about 100 mL/min. The gas composition (CO, CO₂, O₂ and total hydrocarbon) was monitored every 30 s by an analyzer (DJGAS analyzer from De Jaye Technologies) equipped with a non-dispersive infrared (NDIR) sensor. The concentration of the gases was determined by calibrating with standard gas mixtures.

Results and discussion

Test for transport limitations

Initial experiments were performed to obtain conditions necessary to avoid transport limitations. Acetic acid was used as probe molecule. Acetic acid conversions were kept relatively low provided that good control could be achieved. Transport limitations were studied by varying the linear velocity within the bed and catalyst particle size.

Figure 15a represents the effect of linear velocity while keeping a constant contact time. In this test the linear velocity is increased with higher flow rates though the same diameter and void space. It can be seen that there was a turning point between F/W and 2F/2W where at the former there was a decrease in the conversion likely due to bulk diffusion limitation. Further increase in linear velocity resulted in a constant conversion.

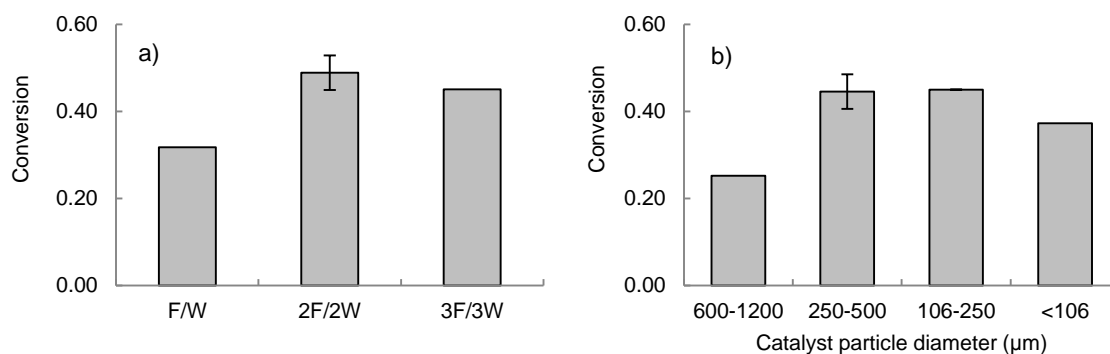


Figure 15 a,b. Tests for transport limitations with acetic acid as probe molecule; F represents feed flow rate of 3.0 mL/hr, W represents 25 mg of catalyst (Sud Chemie Reformax 106-250μm), conversion based on disappearance of reactant

In Figure 15b, a limiting effect was observed for the largest catalyst particles. The results suggest pore diffusion resistance or even channeling within the bed. The smallest particles tested would quickly plug the reactor due to carbon deposition. Based on this analysis the conditions selected for the kinetics tests were using 50 mg of catalyst with feed flow rate of 6.0 mL/hr (2F/2W) and catalyst particle size between 106 and 250 μm.

Model species relative reactivity

The relative reactivity study was based on ease of conversion over the reforming catalyst in terms of reactant disappearance. The previously described reaction conditions allow obtaining data that is relevant to kinetically controlled reactions and products as opposed to equilibrium products. This way the results describe the behavior of the model species relative to one another on the reforming catalyst.

From the results presented in Figure 16a furfural roughly seems like the molecule most resistant to reaction while levoglucosan, acetic acid and glycolaldehyde were the easiest to react. At 460 °C the extent of reactant disappearance seems to just start coalescing. Levoglucosan showed the highest conversion rate among the species tested. Furfural seems to be the most resistant to reaction but these results could be explained with its low concentration since it is possible that the water vapor can start to compete for the active sites on the catalyst surface.[23]

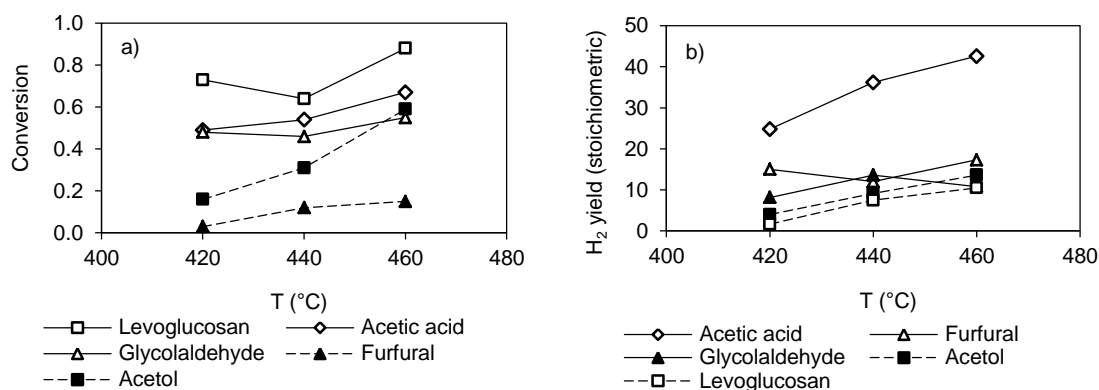


Figure 16 a) Overall conversions of model species during steam reforming reactions, b) hydrogen yields for the same reactions; lines added as visual aids, S/C of 6 (furfural S/C=19), Sud Chemie Reformax catalyst

The results were mostly in agreement with trends in activation energies obtained from the Arrhenius relationship. Furfural had the highest energy barrier at 44 kcal/mol, followed by acetol at 33 kcal/mol, then glycolaldehyde, levoglucosan and acetic acid with 24, 19 and 17 kcal/mol respectively.

The hydrogen yields compared to stoichiometry (Figure 16b) show a different pattern to that seen for the conversions. In this case acetic acid is the molecule with the highest selectivity towards hydrogen topping at around 40% at the highest temperature. Furfural seemed to be the second molecule with the highest hydrogen generation but only at the lowest temperature. Most of the other species top at around 20% towards the highest temperature. It must be noted that levoglucosan was the lowest hydrogen forming species while it was the one with the highest conversion rate. This behavior suggests that the levoglucosan may be more likely to proceed through different reaction pathways generating, for example, solid carbon. It is important to note that some of the carbon forming reactions may also generate portions of hydrogen, thus it is possible to observe hydrogen formation even when high quantities of carbon are produced. An important caveat must be considered while interpreting reactivity data since a higher reactivity could point to a high tendency towards side reactions and carbon deposition.

Carbon deposition study

An example TPO profile from the deposits accumulated from acetic acid steam reforming at 420°C is presented on Figure 17. The points correspond to total concentration of carbon oxides generated during the temperature program. A large peak can be observed at around 450°C with a shoulder around 550°C showing the maxima in coke activation by oxygen evidencing a minimum of two coke species. When compared to literature values from hydrocarbon coke these peaks coincide with carbon characterized as amorphous carbon.[24] Generally the carbon deposits from all model species tested could be described in a similar fashion. This kinetically favored deposition can be quantified to compare the different model compounds.

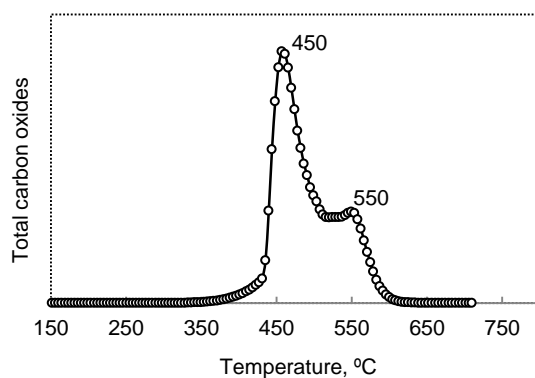


Figure 17. TPO profile from SR of acetic acid at 420°C, S/C of 6.0, Sud Chemie Reformax catalyst

For each reaction the TPO curves were integrated with respect to time and flow rate as measured with the bubble meter to give total moles of carbon accumulated in the reactor. These values were used to determine the solid carbon selectivity from steam reforming. The selectivity represents the mol percent of carbon accumulated with respect of the total carbon products generated including the product gas stream (Eqn. 14). Figure 18a shows the solid carbon selectivity for the selected model species during SR at the three temperatures of interest.

Selectivity to solid carbon:

$$C_s / (C_s + CO + CO_2 + CH_4) \times 100 \quad (\text{Eqn. 14})$$

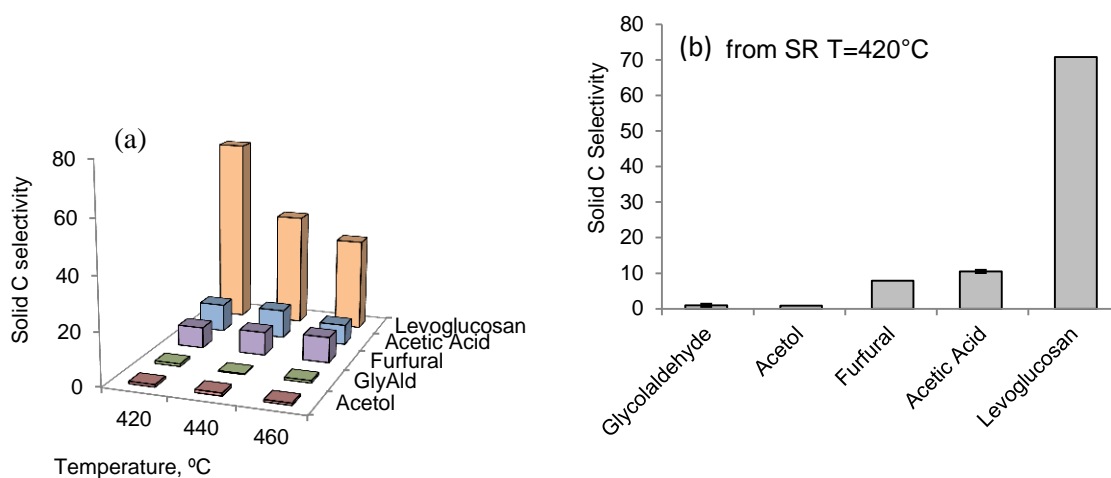


Figure 18 a) Catalytic steam reforming carbon deposition, b) detailed results at 420°C; S/C of 6 (furfural S/C=19), Sud Chemie Reformax catalyst, error bars denote standard deviation from replicates

Levoglucosan appeared largely to be the molecule most prone to carbon deposition followed by acetic acid, furfural, glycolaldehyde and acetol. In general the extent of carbon deposition seemed to be roughly proportional to the molecular weight and length of carbon chain (C_n) of each species for the temperature range tested. This trend is similar to what has been observed for hydrocarbon reforming where the longer the carbon chain of higher hydrocarbons led to carbon precursors arising from dissociative adsorption.[25] Acetic acid is one of the smallest (or simplest) molecules studied but it clearly deviates from the aforementioned behavior. Acetic acid generated the overall second highest amount of carbon deposits. This analysis makes levoglucosan and acetic acid key molecules of interest.

An important question must be answered as to whether the carbon deposits observed with the reforming catalyst are due to catalyst mediated coking or simply by activation in the hot vapor phase or over the reactor surfaces. Non-catalytic or blank runs were performed for all selected model species by packing a bed of inert low surface area SiC pellets over quartz wool.

The average disappearance fractions for the non-catalytic runs were 0.73, 0.47, 0.05, 0.03, and 0.0 for levoglucosan, glycolaldehyde, acetol, acetic acid, and furfural respectively. This trend in activation matches the carbon deposition detected as shown in Figure 19. This figure

shows a solid carbon yield, from the total carbon input to the reactor, instead of solid carbon selectivity since only small traces or no gaseous carbon products were detected. This test represents as a base case that provides insight about the contribution of purely thermal reactions during SR of these oxygenates.

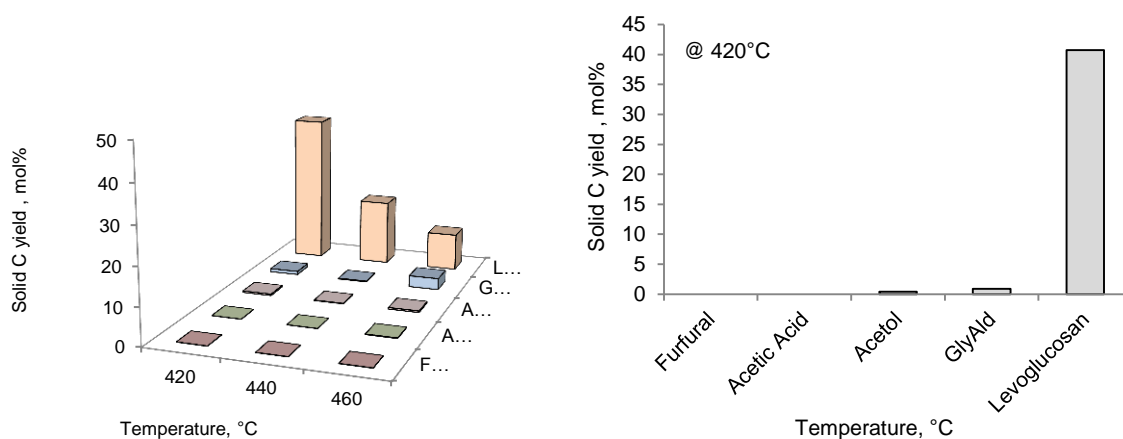


Figure 19. Non-catalytic steam reforming carbon deposition, S/C of 6.0 (furfural S/C=19)

In this case levoglucosan had a far larger extent of carbon deposition from non-catalytic reactions than the other species. If we compare this behavior to the catalytic SR it can be concluded that relative to lighter oxygenates the levoglucosan has a much higher tendency to activate upon heating to generate large amounts of carbon deposits.

No significant activation was observed from furfural, acetic acid, and acetol relative to the levoglucosan during non-catalytic tests. Glycolaldehyde showed a relative high level of disappearance but generated only trace amounts of carbon or even gaseous products. This discrepancy could arise from the ability of this molecule to be present as monomer or dimer, making difficult the quantification in the condensates. Overall when comparing the catalytic and non-catalytic runs it can be observed that carbon deposition from most model species, except levoglucosan, is related to activation over the reforming catalyst in the temperature range studied. This type of carbon deposition is more closely identified as catalytic coking as described in hydrocarbon reforming literature.[24-26]

There also seems to be a pattern of decreasing carbon deposition from levoglucosan as the temperature increases from 420 to 460°C in both catalytic and non-catalytic results. It is unclear whether this was a result of higher heating rate due to temperature gradient or from shorter residence time. This also coincides with observations that levoglucosan is stable at fast pyrolysis conditions if there exists a rapid heating rate combined with short residence times in the magnitude of seconds.[27]

If we consider the disappearance of levoglucosan to arise from pyrolysis within the reactor it could be expected that it would generate low molecular weight oxygenates like acetic acid, acetol and glycolaldehyde without significant char or carbon deposition.[27] Based on the results presented in this work, individual contribution from these lighter species do not add up to the deposits observed from levoglucosan itself. Interaction effects between these molecules cannot be ruled out nonetheless. Conversely, the anhydrosugar may activate over generally inert surfaces or even the vapor phase to form larger molecules. Oligomers formed could clearly act as precursors for carbon deposits.

Acetic acid

Further investigation of acetic acid carbon deposition was performed to obtain insight into the effect of functionality on catalyst coking. The first objective of the following test was to study coking tendency from an acetic acid intermediate and the second to study different carboxylic acids to try to deconvolute the effect of the carboxylic moiety.

Some amounts of acetone were observed in the condensates after steam reforming of acetic acid. Acetone is a likely intermediate product from this reaction. It has been reported that acetic acid can ketonize[11,19], especially on reactive support materials.[14] It has been discussed in the past that acetone is prone to polymerization over acidic catalysts.[28]

Acetone was steam reformed under same set of conditions at 420 and 460°C to test coking tendency. Quantification of coke deposits from acetone compared to acetic acid is presented in Figure 20. Acetone generates a comparable amount of coke to that of acetic acid. It must be noted that acetone in turn may generate acetic acid as an intermediate due to

decomposition reaction. Results in the literature support the idea that a main pathway for coke generation from acetic acid SR is due to formation of oligomers from acetone on acid sites of the support materials.[14,18]

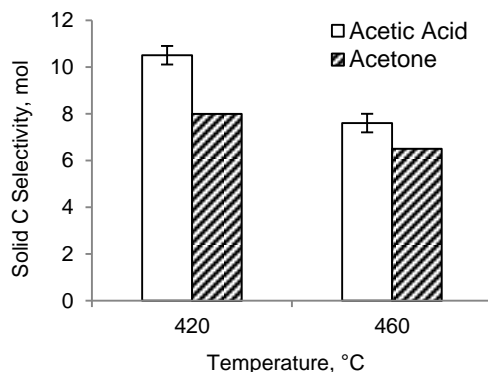


Figure 20. Catalytic coking comparison for acetic acid and acetone, S/C=6

Other carboxylic acids like formic acid and propionic acid were tested to try to understand the acid functionality effect on catalytic coking. The difference between these molecules lies on the length of the carbon chain from the carboxylic carbon. This test unveils a different point of view since the acids may not have the same tendency to ketonize as observed with acetic acid. For example, additionally to what discussed before for acetic acid, formic acid(C_1) may not ketonize and propionic acid(C_3) may ketonize to 3-Pentanone. The results from steam reforming of formic acid showed only a small trace of coke deposited on the catalyst (Figure 21). Formic acid is an interesting molecule since it only contains one carbon atom that is already in a high oxidation state, therefore the formation of CO_2 does not require C-C bond breaking leaving minimal chance of polymerization. Similarly the potential for H_2 production from formic acid is very low and can only come from the water-gas shift component of the reaction.

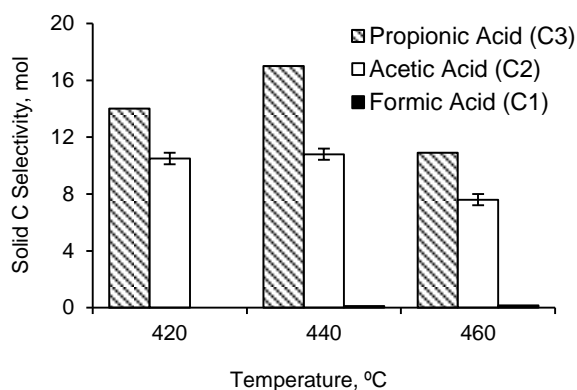


Figure 21. Carboxylic acid coke deposition study

Propionic acid is a slightly larger molecule with one additional carbon in the chain connected to the carboxylic group when compared to acetic acid. The results for propionic acid showed that the coking tendency was even higher than that observed from acetic acid. An important observation when comparing formic acid to acetic and propionic acid is that the way these acids react has an important effect more related to C-C bond activation and not necessarily from the interaction of the carboxylic group with the catalyst. The C-C bond activation relates to the generation of ketones as coke precursors over the catalyst.

Acetic acid comes through as a key molecule to study since not only is it a problem species but also one of the most abundant molecules in the water-soluble portion of bio-oils. This is even more true in systems where acetic acid enrichment can be achieved by, for example, fractionation (see Chapter 3). With the possibility of displacing the carbohydrates from these types of bio-oil fractions we would face with acetic acid being the troublesome species in terms of catalyst coke. Therefore new insight from acetic acid coking over the reforming catalyst that is collected can become useful to address the overall coking issue of this kind of bio-oil fraction. Conversely the issues associated with levoglucosan and perhaps other carbohydrates were not that strongly related to the catalyst. This could prove that issues associated with carbohydrate rich bio-oils can be addressed by other means like reactor design or condensed phase processing.

Conclusions

It was found that the anhydrosugar (levoglucosan), the carboxylic acid (acetic acid) and the light aldehyde (glycolaldehyde) reacted more readily at temperatures between 420-460°C. Levoglucosan showed the highest carbon deposition followed by the acetic acid and furfural. Among the model species tested the levoglucosan converts more readily towards carbon deposits largely through non-catalytic activation. These reactions could be associated with pyrolysis or polymerization reactions. The challenge for SR or the anhydrosugar lies in the reactor design and reaction conditions but not as strongly on catalyst selection.

The tendency to generate solid carbon increased with the carbon chain length and complexity of the molecules. Acetic acid and furfural, as some of the most relevant chemicals generated from fast pyrolysis of biomass, were major coke forming species during steam reforming. These results clearly point now to the potential in catalyst design to help mitigate this issue.

Acetic acid readily cokes via the formation of coke precursors from ketone intermediates. By comparing the results from acetone and propionic acid reforming it can be concluded that not only carboxylic acids are particular coke forming species but the coke formation is related to the amount of C-C bonds that need to be cleaved.

From these results acetic acid, acetone, or even furfural seem to be good probe molecules to represent the troublesome high coke forming species in aqueous bio-oil. Acetic acid stands out as being the problem species most abundant in typical water-soluble bio-oils. Further research can focus on targeting the fundamental limitations of the interaction between acetic acid and the reforming catalyst. Further insight on acetic acid coking could have a strong impact on overall coking properties from water-soluble bio-oils and especially from acetic acid enriched bio-oil fractions.

Acknowledgment. This work was performed with the support of the U.S. Department of Agriculture, project number 68-3A75-5-233.

References

1. Oasmaa A, Czernik S: Fuel Oil Quality of Biomass Pyrolysis Oils-State of the Art for the End Users. *Energy Fuels* 13(4), 914-921 (1999).
2. Mohan D, Pittman CU, Steele PH: Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* 20(3), 848-889 (2006).
3. Oasmaa A, Kuoppala E, Solantausta Y: Fast Pyrolysis of Forestry Residue. 2. Physicochemical Composition of Product Liquid. *Energy & Fuels* 17(2), 433-443 (2003).
4. Huber GW, Corma A: Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass. *Angewandte Chemie International Edition* (46), 7184-7201 (2007).
5. Bridgwater AV, Cottam M-L: Opportunities for Biomass Pyrolysis Production and Upgrading. *Energy & Fuels* 6(2), 113-120 (1991).
6. Kechagiopoulos P., E. Vagia, A. Iordanidis, S. S. Voutetakis, A.A. Lemonidou, Vasalos IA: Hydrogen production from renewable energy sources: reforming of biogas and bio-oil. *Catalysis, Energy and Environment. Workshop of CPERI*, (2004).
7. Kechagiopoulos P.N., Voutetakis S., Lemonidou A., I AV: Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-oil in a Fixed Bed Reactor. *Energy and Fuels* (20), 2155-2163 (2006).
8. Basagiannis AC, Verykios XE: Steam reforming of the aqueous fraction of bio-oil over structured Ru/MgO/Al₂O₃ catalysts. *Catalysis Today* 127(1-4), 256-264 (2007).
9. Czernik S, Evans R, French R: Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catalysis Today. Recent Advances in Catalytic Production of Hydrogen from Renewable Sources* 129(3-4), 265-268 (2007).
10. Wang DN, Czernik S, Chornet E: Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. *Energy & Fuels* 12(1), 19-24 (1998).
11. Wang D, Montane D, Chornet E: Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde. *Applied Catalysis a-General* 143(2), 245-270 (1996).
12. Basagiannis AC, Verykios XE: Reforming reactions of acetic acid on nickel catalysts over a wide temperature range. *Applied Catalysis A: General* 308, 182-193 (2006).
13. Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R: Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Applied Catalysis B: Environmental* 61(1-2), 130-139 (2005).
14. Takanabe K, Aika K-I, Seshan K, Lefferts L: Sustainable hydrogen from bio-oil-- Steam reforming of acetic acid as a model oxygenate. *Journal of Catalysis* 227(1), 101-108 (2004).
15. Galdamez JR, Garcia L, Bilbao R: Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni-Al Catalysts. Acetic Acid as a Model Compound. *Energy Fuels* 19(3), 1133-1142 (2005).
16. Garcia L, French R, Czernik S, Chornet E: Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Applied Catalysis A: General* 201(2), 225-239 (2000).

17. Iojoiu EE, Domine ME, Davidian T, Guilhaume N, Mirodatos C: Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia. *Applied Catalysis A: General* 323, 147-161 (2007).
18. Takanabe K, Aika K-I, Inazu K, Baba T, Seshan K, Lefferts L: Steam reforming of acetic acid as a biomass derived oxygenate: Bifunctional pathway for hydrogen formation over Pt/ZrO₂ catalysts. *Journal of Catalysis* 243(2), 263-269 (2006).
19. Hu X, Lu G: Investigation of the steam reforming of a series of model compounds derived from bio-oil for hydrogen production. *Applied Catalysis B: Environmental* 88(3-4), 376-385 (2009).
20. Markevich M, Czernik S, Chornet E, Montane D: Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil. *Energy Fuels* 13(6), 1160-1166 (1999).
21. Wang D, Czernik S, Montane D, Mann M, Chornet E: Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. *Industrial & Engineering Chemistry Research* 36(5), 1507-1518 (1997).
22. Piskorz J, Scott DS, Radlein D: *Pyrolysis Oils from Biomass*. In: E. J. Soltes and T. A. Milne, ACS Symposium Series 376. Washington, DC 1988.
23. Markevich M, Medina F, Montané D: Hydrogen production via steam reforming of sunflower oil over Ni/Al catalysts from hydrotalcite materials. *Catalysis Communications* 2(3-4), 119-124 (2001).
24. Tian L, Zhao XH, Liu BS, Zhang WD: Preparation of an Industrial Ni-Based Catalyst and Investigation on CH₄/CO₂ Reforming to Syngas. *Energy & Fuels* 23(2), 607-612 (2009).
25. Trimm D: Catalysts for the control of coking during steam reforming. *Catalysis Today* 49(1-3), 3 (1999).
26. Le Page JF: *Applied heterogeneous catalysis : design, manufacture, use of solid catalysts*. Éditions Technip, Paris. (1987).
27. Patwardhan PR, Satrio JA, Brown RC, Shanks BH: Product distribution from fast pyrolysis of glucose-based carbohydrates. *Journal of Analytical and Applied Pyrolysis* 86(2), 323-330 (2009).
28. Egret H, Couvrecelle J-P, Belleney J, Bunel C: Cationic polymerization of dimethyl ketene. *European Polymer Journal* 38(10), 1953-1961 (2002).

Chapter 5. Steam Reforming of Acetic Acid over Mg and Co modified Ni/Al₂O₃ catalyst

A manuscript to be submitted to the *Energy and Fuels* Journal

Pedro J. Ortiz-Toral^{1,2}, Martin K. Dufficy¹, Robert C. Brown^{2,3}, and Brent H. Shanks^{1,4}

Abstract

Acetic acid is one of the most abundant species in water-soluble bio-oil produced from fast pyrolysis of biomass. Among these species it has been selected as a probe molecule, identified previously as one of the most prone to coking during catalytic steam reforming over Ni/Al₂O₃ catalyst. Mg and Co modified Ni/Al₂O₃ steam reforming catalysts were tested at 460 and 650°C. These temperatures correspond respectively to reforming regimes where no coke steam-gasification was observed and where coke steam-gasification happened at an accelerated rate as determined by temperature programmed coke removal by steam. The addition of Mg as support modifier led to reduced coke accumulation by promoting coke gasification at 650°C, but at 460°C a different trend was observed where coke gasification rate was not prevalent. A supported bimetallic NiCo catalyst showed a coke hindering effect at 460°C, but at 650°C it seemed to promote coke formation. The presence of an Al₂O₃ support was shown to be necessary to achieve high hydrogen formation with decreased coking. The data suggests that a synergistic effect exists between the NiCo and the Al₂O₃ support, where the latter may enhance water activation contributing to the reduced coking for the bimetallic catalyst.

¹Department of Chemical and Biological Engineering,

²Center for Sustainable Environmental Technologies,

³Department of Mechanical Engineering; Iowa State University, Ames, Iowa 50011

⁴Author for correspondence: bshanks@iastate.edu

Introduction

The accumulation of carbon deposits has been identified as the most considerable limitation to the production of hydrogen from water-soluble fast pyrolysis bio-oil via steam reforming (SR). The generation of these deposits compromises the hydrogen yield and can lead to catalyst deactivation.[1] Bio-oil in general is a complex mixture of numerous oxygenated hydrocarbons arising from the different components of lignocellulosic biomass.

Consequently the chemistry of different molecules may greatly influence the SR properties.

To further understand bio-oil's properties, we need a thorough understanding of the behavior of individual components during SR.[2] Acetic acid is one of the most abundant species in bio-oil.[3-6] It has been identified as a problem species of catalyst coking during SR (previous chapter). Acetic acid can be tested as a coking probe molecule using catalysts with modified properties to study carbon deposition hindering while maximizing hydrogen production. Improvements in coking from acetic acid could have a substantial impact on the overall coking from bio-oil SR.

The mechanism for catalytic coke formation could be very complex due to the number of reactions and reaction sequences that can lead to oligomer deposition or surface carbon polymerization.[7] Some of the pathways may arise from the nature of specific oxygenated species in bio-oil while others could correspond to the coking phenomena observed with hydrocarbon SR. One relevant pathway that has been discussed is related to the generation of intermediates that work as coke precursors on acid sites of the catalyst support.[5,8] Coke formation has been demonstrated to be a function of acid-base properties of the catalyst and its interaction with the reactants.[7] Acetic acid, for example, has been shown to ketonize and then oligomerize on acid sites of the catalyst support forming coke by oligomer condensation.[8]

The acid/base support in a SR catalyst plays a role in activating the steam molecules which later react with the metal adsorbed species at the metal-support interface.[1,8] The acidity of a support material can greatly depend on the nature of adsorbed species.[9] An acid functionalized support material like Al_2O_3 can promote cracking and dehydration reactions

that could lead to the formation of coke precursors.[10-12] This property of the Al_2O_3 , can contribute to the overall conversion of the feedstock. Defunctionalizing a reforming support could result in an apparent decrease in overall activity of the catalyst.

Another pathway that has been discussed is the polymerization of surface carbides generated during dissociative adsorption of the molecule on the active metal.[13-15] As it has been discussed mostly for hydrocarbon SR, this can be attributed to accelerated C-C bond breaking on the metallic phase of the catalyst. Excess surface carbides provided by the metal can polymerize leading to stable coke deposits.[13]

Several different approaches to minimize the overall carbon deposition from bio-oil and bio-oil model compounds have been discussed in the literature. It has been generally discussed that by introducing high S/C molar ratios higher than 8 [1,16] combined with elevated temperatures, the extent of carbon accumulation could be limited by steam gasification of these deposits. [17-24] However, besides focusing on carbon removal it is also important to explore methods that minimize the formation of coke deposits.

Typical SR of oxygenated species is performed at temperatures much lower than those needed for hydrocarbon SR (around 800°C).[25,26][1,18] Lower SR temperatures favor the exothermic water-gas shift (WGS) reaction for maximum hydrogen productivity. Based on the two pathways mentioned above there is room to study different alternatives to try to achieve this, especially at lower temperatures.

There is a potential way to modify the acidity –reducing acid site strength or reducing the concentration of acid sites- by the addition of a basic material like an alkaline or alkaline-earth mineral. A desirable additive or modifier should not inhibit the adsorption of water molecules or the transport of these to the SR active sites.

Modifying the properties of an active metal like Ni, instead, is possible via the addition of a second metal so that either an alloy or spinel is formed. This type of bimetallic catalyst may adjust the C-C cleavage property to control the generation of coke precursors.[13]

Magnesium addition

As mentioned above, it has been proposed that the acidic property of alumina favors undesired reactions from SR of oxygenates leading to catalyst coking. Such hypothesis has been tested for SR of ethanol, where an acid support promotes dehydration reactions leading to coke formation. [27-30]

Mg modified reforming catalyst has been designed to increase hydrogen production by neutralizing acid sites on the support and controlling the rate of coking. In this case a Mg modified catalyst showed a reduced formation of the dehydration product (ethylene) from ethanol SR with a consequent reduction in coke accumulation at temperatures around 650°C. Basic supports like MgO have been shown in the past to reduce the rate of carbon deposition from ethanol SR when compared to acidic supports.[31] A Ni/MgO/Al₂O₃ catalyst has been compared with a Ni/Al₂O₃ for SR of acetic acid. [32] It was suggested that carbon deposition and ketonization of acetic acid were depressed at SR temperatures between 650 and 800°C.

Mg modification of a reforming catalyst has also been investigated in the CO₂(dry) reforming of methane.[33,34] For this reaction, Ni metal supported on mixed Mg and Al support (33 mol% Mg) has been shown to limit coke formation with high activity at temperatures between 650 and 750°C.[34] Mg addition has also been mentioned to enhance the retention of carbon dioxide which in turn prohibited the formation of carbon deposits during CO₂(dry) reforming of methane.

The ability of steam absorption has been related to the extent of coke generation. [17] It was also suggested that the presence of Mg may enhance the steam adsorption on the catalyst leading to the increase in steam gasification of coke.[1,35] The ability of the alkali to catalyze steam gasification reactions at these elevated temperatures may be key to improving the accumulation of carbon deposits.[20,36] It is important to systematically investigate if a catalyst support can be modified to hinder coke formation at low SR temperatures or to simply promote steam gasification of the deposits at elevated temperatures.

Cobalt addition

Ni and Co based catalysts have been previously explored for ethanol SR with some success in improving selectivity by reducing methane formation.[37] The addition of Co to a reforming catalyst has resulted in improvement in the activity and dispersion of active metal.[38-40]

Bimetallic NiCo based catalysts have recently become attractive for SR of acetic acid at low temperatures.[41] An unsupported bimetallic NiCo catalyst at an ion ratio of 1:4 has been found to be very active in terms of ease of conversion of acetic acid at temperatures between below 500°C. Complete conversions were achieved at these temperatures for this catalyst formulation given by a low space velocity ($LHSV = 5.1 \text{ h}^{-1}$) and a relatively high S/C of 7.5. This particular catalyst formulation showed the best selectivity in terms of low generation of CO and CH₄ byproducts. In this single study addressing acetic acid SR at low temperatures the NiCo catalyst formulation allegedly generated a combined level of coke and acetone formation attributing to less than 1% of the carbon balance.[41]

An interesting hypothesis is that the Co addition to a Ni catalyst may modify the reactivity in terms of C-C bond cleavage and WGS, among other modifications.[15,42] Co addition may modify the C-C bond cleavage property of Ni metal to help control the generation of surface carbides leading to coke[14], but may not necessarily promote the removal of coke as it could be the case in Mg modification of the reforming catalyst.[43,44] It has been also discussed that Co may promote adsorption and/or mobility of oxygen containing species to modify the Ni activity.[14,42] For this reason it could be speculated that Co may serve as a surface modifier capable of promoting the adsorption of water molecules for SR without the need of surface expression of the support material. A clear next step will be to test a supported bimetallic NiCo catalyst for this application to test the effect of the support material which has been discussed to be important part of the acetic acid reforming reaction.[8]

This study analyzes catalyst stability in terms of catalyst coking from acetic acid as a problematic bio-oil species acknowledging that other catalyst deactivation pathways may exist. In order to focus on coke formation, the extent of coking was measured directly and not

based on times-on-stream. This type of study can be performed later once reaction regimes are defined and appropriate catalyst modifications are studied.

Experimental

Two sets of reforming catalysts were synthesized for this work based on Ni/Al₂O₃ as baseline. One set was based on the Mg modification of the support material and another set based on Co addition for the bimetallic catalyst. The catalysts were characterized to study resulting surface areas, metal dispersions, and to identify metallic phases. The catalysts were then tested in a SR reactor to study hydrogen production and carbon deposition.

Catalyst synthesis

Mixed and pure alumina and magnesia supports were prepared by aqueous precipitation method of nitrate precursors based on what presented on Coleman et al.[44] The supports prepared were 100% Al, 30%Mg/70%Al, and 100% Mg on a mol basis. The nitrates used for supports were Al(NO₃)₃·9H₂O (99+%, Acros Organics) and Mg(NO₃)₂·6H₂O (≥99.0%, Sigma Aldrich). For each batch of support, 250 mL of a 1M aqueous nitrate solution was added drop-wise into a beaker containing 250 mL of 0.5M aqueous Na₂CO₃ (ACS grade, Fisher) solution. The precipitation solution was kept at a constant pH of 10 by adding a 3M NaOH solution using a buret. The beaker was vigorously stirred and kept at room temperature throughout the precipitation process. The precipitates were aged for 12 hr at 65°C while stirring. The precipitates were then dried at 110°C overnight and calcined in air by ramping the temperature up to 850°C and holding that temperature for 5 hr. The support materials were then crushed and sieved to 106-250 μm.

Ni addition was done by incipient wetness method with a 2M Ni(NO₃)₂·6H₂O (ACS grade, Fisher) solution. A 3M total ion concentration of Ni and Co (Co(NO₃)₂·6H₂O) nitrate solution was prepared for impregnation of the supported bimetallic catalyst. The Ni:Co ratio was set to 1:4 based on the ion ratio.[41] An unsupported NiCo material was also synthesized at this same ionic ratio by precipitation method based on the procedure on Hu et al.

The resulting materials were dried overnight and calcined in air by ramping the temperature up to 750°C and holding that temperature for 5hr. The impregnation was performed two times in the case of Ni and three times for NiCo. The materials were then sieved once more between 106-250 μm . The catalysts were reduced prior to reforming tests for 4 hr with 50/50 H_2 and N_2 gas mixture at 550°C.

Catalyst characterization

The BET surface area of the prepared materials was determined by nitrogen physisorption (Quantachrome NOVA 4200e Gas Sorption Analyzer). The active metal surface area was determined by H_2 -pulse-chemisorption (Mircromeritics 2920). For the chemisorption tests, unreduced catalyst samples were reduced for 4hr with diluted hydrogen gas at 550°C. The cell was then cooled down while purging with inert gas. Analysis was performed at 50°C. Metallic surface area and dispersion were determined from the metal loading on the catalysts.

Temperature programmed oxidation with air (Air-TPO) was performed after the reforming reactions to study the coke deposits on used catalysts. After each reforming test the reactor was purged with N_2 while cooling down to approximately 110°C. The reactor was held at this temperature enough to desorb moisture and carbon species like CO_2 . The temperature was ramped from 110°C to 720°C at a rate of 8 °C/min while running air through the reactor. The temperature was held at 720°C until no further carbon was detected.

For the TPO tests, the gas composition (CO , CO_2 , NO_x , and O_2) was monitored with a real-time analyzer (De Jaye Technologies DJGAS) equipped with a non-dispersive infrared (NDIR) sensor. The concentration of the gases was determined by calibration curves from standard gas mixtures. The total gas flow rate was monitored throughout the tests using the bubble meter. The response curves of the oxidation products CO and CO_2 (CO_x) can be integrated and added to yield the total number of moles of carbon accumulated.

Reaction setup

Steam reforming experiments were performed using a tubular fixed bed reactor setup elsewhere described in more detail (see Chapter 3). The liquid feed flow rate was set at 6.0

mL/hr providing a drop over the bed surface approximately every 8 s. Nitrogen gas was fed as a sweep gas and an internal standard at 60.0 mL/min. The liquid feed was injected no more than 4 cm above the top of the catalyst bed using a 0.8 mm inner diameter capillary tube with a diagonal cut at the tip. To prevent direct radiation from the furnace to prevent plugging by carbon deposits, the entire length of the injector was shielded with ceramic wool. Quick contact of the feedstock and the catalyst while minimizing preheating.

The catalyst was packed on top of a quartz wool plug and supported by a quartz frit located near the vertical center of the reactor. The bed was packed with 50 mg of prepared catalyst together with inert SiC material, which improved heat and transport properties. Fresh catalyst was used for each reaction to eliminate the effect of catalyst stability.

The top and bottom sections of the reactor were heated by heat tapes set at 140 °C to prevent condensation. Condensates were collected into two condensers in a salt-ice bath. Methanol was used as bubbling media to improve the efficiency of the catch. Any moisture left in the gas stream was removed by flowing through a Drierite filter. A slip stream of the effluent was analyzed by in-line GC. The total flow rate of the effluent stream was measured continuously using a volumetric bubble flow meter which was connected to a vent.

Acetic acid (ACS grade, Fisher) and DI water were premixed and fed through a single syringe injection tube using a syringe pump (KD Scientific). The solution was prepared to be $21.74 \pm 0.01\%$ acetic acid corresponding to a S/C of 6.0. A total of 8.0 mL of solution was injected to the reactor per run at a rate of 6.0 mL/hr.

The gas stream exiting the reactor was sampled and analyzed approximately every 3-4 minutes by a Varian CP-4900 MicroGC. The evolution and steady-state concentrations of H₂, CO₂, CO, CH₄ gases were determined by calibration curves from gas standards. The water-rich condensate samples were analyzed by a GC (Agilent) equipped with a 30 m long DB-624 column and an FID detector.

Preliminary tests were performed to determine appropriate temperatures for the coking study. The study was based on steam-TPO of a coked Ni/Al (Ni/Al₂O₃) catalyst. Two SR

temperature regimes where defined to deconvolute coke gasification regime from purely coke accumulation.

In situ temperature programmed oxidation with air (Air-TPO) method was performed to quantify the carbon deposits from steam reforming including on reactor surfaces. The procedure used was based on the method used on Tian et al.[45] For this analysis the reactor was cooled down after each reaction to approximately 110°C while purging with N₂ flow. The reactor was held at this temperature for about 15 min or however necessary to remove moisture and physisorbed gaseous species like CO₂ from the system. For the TPO the temperature was ramped from room temperature to 720°C at a rate of 8 °C/min under flow of air at about 100 mL/min. The gas composition (CO, CO₂, O₂ and total hydrocarbon) was monitored every 30 s by an analyzer (DJGAS analyzer from De Jaye Technologies) equipped with a non-dispersive infrared (NDIR) sensor. The concentration of the gases was determined by calibrating with standard gas mixtures.

Results and discussion

Determination of temperature regimes for coking study

The temperature programmed removal of coke by steam is presented on Figure 22. This figure shows the temperature profile of the carbon deposits from acetic acid SR removed by steam gasification up to a temperature of 720°C. The steam gasification activity started approximately at 550°C and peaked at roughly 650°C. At temperatures below 550°C there was no detectable carbon removal from the catalyst. However, above 550°C, an increase in steam gasification activity was observed, and perpetuated until the carbon was completely removed.

On the steam-TPO profile, the peak at 650°C shows a clear point of accelerated coke gasification. A high SR temperature like 650°C under excess steam may provide conditions favoring coke removal by steam that could mask any coke hindering effects.

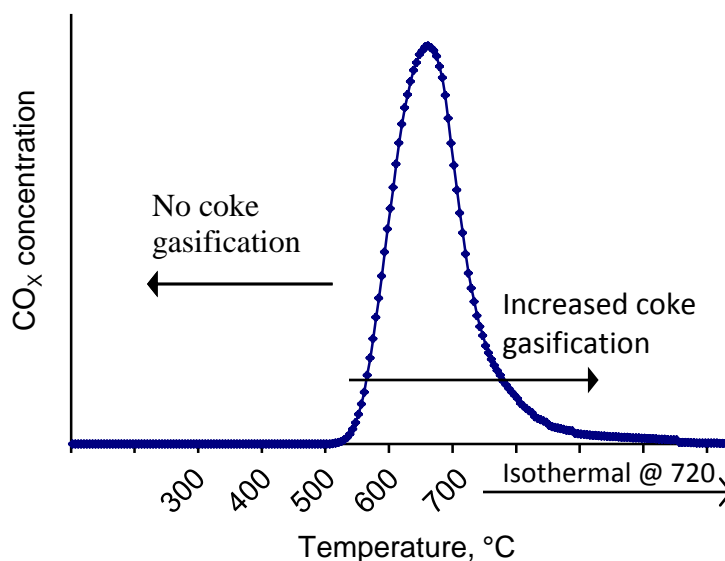


Figure 22. Steam-TPO of carbon deposits after acetic acid SR at 460°C over Ni/Al catalyst

This gasification activity may especially increase with the addition of basic properties to the support.[28,44] Considering that this reaction will occur during SR at these temperatures it is difficult to differentiate the coke gasification by steam from any improvements that can be achieved in coke formation inhibition.

A temperature like 460°C is a key temperature where high amounts of coke have been detected from acetic acid SR (see Chapter 4). From the figure, there was no perceivable coke removal at this temperature. It can be concluded that at a temperature of 460°C, any amount of coke accumulated from acetic acid SR cannot be removed by the excess of steam. At this low temperature it would be possible to deconvolute the formation of coke from the rate of coke removal by steam.

The Ni/Al baseline reforming catalyst and the modified catalysts synthesized were subsequently tested at two key temperatures (460 and 650°C) defined by the temperature regimes from the steam-TPO of coke. The goal is to study possible enhancement at either of both temperatures according to the effect of the additive.

Mg modification

The physicochemical characterization of the prepared catalysts is shown on Table 6. For the impregnated catalysts, the total metal loading of all catalysts was kept between 10-14 wt%. The metal loadings were determined gravimetrically based on the final weight after calcination. The BET surface area varied between 30 and 130 m²/g. The BET surface area seemed to be influenced by the composition of the support as well as the nature of the impregnated metal.

In the case of metal dispersion, the lowest value was for the Ni/30MgO/Al catalyst while the highest value corresponded to the Ni/MgO. The pure MgO supported catalyst did not show any reduced Ni metal during H₂-TPR up to 900°C (not shown). Regardless of the resistance of this catalyst to reduce the NiO, the H₂ chemisorption analysis showed dispersion and perhaps the appearance of relatively small crystallites. A high metal dispersion seems to suggest that the NiO is somewhat active for H₂ chemisorption.

Table 6. Catalyst characterization by N₂ physisorption (BET S.A.) and H₂ chemisorption

Catalyst	Total metal loading (wt%)	Surface Area (m ² /g)	Active Surface Area (m ² /g cat)	Metal dispersion (%)
Ni/Al	10.5	128	0.324	0.464
Ni/30MgO/Al	11.2	99	0.271	0.363
Ni/MgO	14.0	30	0.581	0.623

The XRD analysis of the catalysts with Mg, Al, and mixed supports is presented in Figure 23. The Ni/Al catalyst shows mostly pure Ni and Al₂O₃ phases, while the Ni/MgO shows strong signals for the oxide NiO and MgO. The MgO clearly inhibits the reducibility of the NiO on the surface.[46] Additionally a MgAl₂O₄ spinel phase appeared for the mixed oxide supported catalyst.

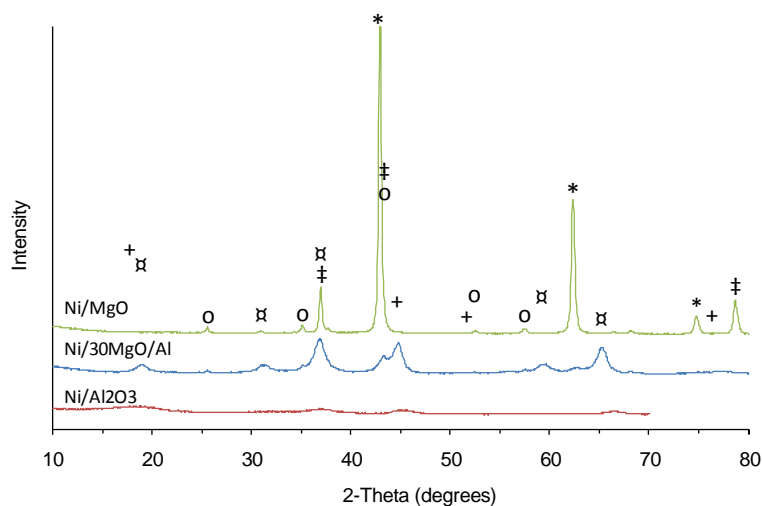


Figure 23. XRD analysis of the reduced Ni catalysts over pure and mixed Al and Mg supports; Ni (+), Al_2O_3 (o), MgO (*), NiO (‡), MgAl_2O_4 (⌘)

A summary of the reaction testing results for Mg modified catalysts is presented on Table 7. The extent of coking relative to hydrogen productivity (moles of C_5 per moles of H_2) is presented for the Ni over pure and mixed supports on Figures 24 (a,b) and 25 (a,b) as a measurement of coke selectivity. At 460°C, it can be observed that the relative coking increased with increasing amount of MgO on the support (Figure 24a). The coking selectivity for the Ni/Al catalyst was somewhat similar to that observed for the Ni/30MgO/Al.

Table 7. SR reaction testing results for Mg modification tests; S/C=6, mass balance 96±4%

	Ni/Al	Ni/30MgO/Al ^a	Ni/MgO	Ni/Al	Ni/30MgO/Al ^a	Ni/MgO
T (°C)	460	460	460	650	650	650
Conversion (mol%)	0.17	0.34	0.10	0.65	0.83	0.63
H_2 (mol/hr)	0.55	1.74	0.11	4.48	5.85	4.41
CO_2 (mol/hr)	0.28	0.97	0.10	2.16	2.80	2.12
CO (mol/hr)	0.09	0.14	0.02	0.36	0.45	0.32
CH_4 (mol/hr)	0.02	0.02	0.00	0.10	0.05	0.06
^b C_5 (mol/hr) * 10^3	0.81	2.99	0.50	1.00	0.97	0.69
$\text{H}_2^{\text{stoich}}$ yield (mol%)	6.5	20.6	1.3	52.9	69.1	52.1
^b C_5 mol/ H_2 mol	0.145	0.181	0.452	0.023	0.017	0.015

^a these values represent averages from replicate

^b C_5 refers to carbon from coke deposits

However these values seemed much lower than what was observed for the Ni/MgO. If we look at the BET surface area, the values for this set of catalysts seem to roughly follow a similar trend where the catalyst with the highest overall surface area seemed to discourage coke formation relative to hydrogen.

Another way to interpret this data is based on an apparent improvement in coke selectivity with increased content of Al_2O_3 in the support and a higher BET surface area. This may suggest that at the low SR temperature, a high concentration of Al_2O_3 sites are needed to promote hydrogen production while keeping coke formation moderate. For instance, the conversion does not follow a particular trend based on BET surface area or even metallic surface area. However it does seem that the mixed oxide supported catalyst had a higher conversion at the lowest active metallic surface area validating the importance of the support composition or even the formation of the spinel.

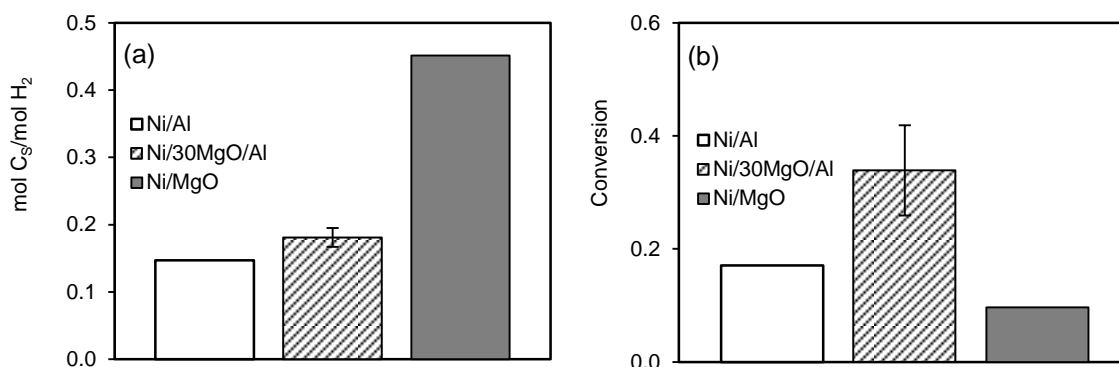


Figure 24. a) Coke as function of hydrogen generation for Ni catalysts over pure and mixed Al and Mg supports, b) Acetic acid conversion; acetic acid SR, at 460°C, S/C=6

At 460°C there was no clear difference in coke selectivity between the Ni/Al and the Mg modified catalysts. The Ni/MgO tended to generate more coke per mol of H_2 while having the lowest apparent activity (Figure 24b). The decrease in conversion for the Ni/MgO catalyst could be related to the lower surface area of this catalyst or even its ability to stabilize the NiO making it difficult to reduce.[46] Furthermore it can be observed that relative to hydrogen productivity there was a reduced formation of CH_4 for the Mg

containing catalysts suggesting the possibility of improved selectivity by suppression of the methanation reaction.

On the other hand at 650°C (Figure 25a), it can be observed that there was a slight decrease in coke selectivity for both Mg containing catalysts. This apparent improvement could correspond to an increased coke gasification rate due to the presence of a gasification promoter. At this temperature the acetic acid conversion for all the catalysts started to converge. This could suggest an effect from approaching thermodynamic equilibrium.

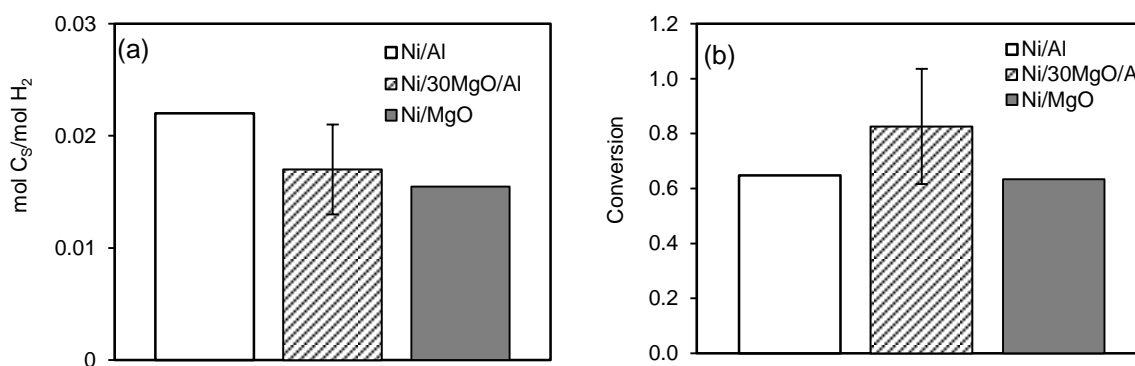


Figure 25. a) Coke as function of hydrogen generation for Ni catalysts over pure and mixed Al and Mg supports, b) Acetic acid conversion; 650°C, S/C=6

In general terms, the Mg containing catalysts showed improved coke selectivity at the high SR temperature. This result corresponded to what has been observed for hydrocarbon reforming, where a MgO oxide support slightly reduced the activity but with a larger improvement in coking. [17] However, this behavior could be explained by improved coke removal along with the reforming reaction at this temperature. The addition of Mg or the use of a MgO support for the SR catalyst did not necessarily showed a positive effect at the low temperature where essentially no coke removal occurs. This suggests that the modified acidity or creation of spinel on the mixed support catalyst did not have a direct impact on the generation of coke. In fact coking appeared to be promoted relative to hydrogen generation with Mg addition.

An effect was observed on coke/H₂ selectivity depending on the Mg content but also on the BET surface area especially at the low SR temperature. In the absence of coke gasification, the catalyst supported on pure MgO performed poorly in terms of acetic acid conversion and coking relative to hydrogen productivity when compared to the Al₂O₃ supported and the mixed support catalyst.

It must be noted that the Ni/Al catalyst showed lower selectivity to coke at the low SR temperature suggesting that the addition of Mg may perhaps hinder hydrogen activity or promote coke forming reactions by the addition of basic sites. These results are not in any way definitive in this matter and require further investigation.

In terms of ketone formation, it was observed that the Mg modified catalysts only generated small traces of acetone at 460°C while the Ni/Al generated about 0.3 mmol/hr of acetone. At 650°C, acetone was detected at around 0.1 mmol/hr for all catalysts. The relationship between ketone formation and coke deposition was not clear from these tests but at the lower temperature acetone formation seemed decrease but at the higher temperature remained more consistent for all catalysts but at a lower value than the low temperature. The impact of acetone formation on hydrogen yield may be insignificant since the generation of these vary by 3-4 orders of magnitude.

Other research has shown that presence of Mg in the catalyst resulted in smaller crystallite sizes with an increase in activity.[47] Mg was found to stabilize nickel by preventing catalyst sintering.[35] Sintering of Ni metal has been also associated with coking in a number of cases at elevated temperatures. [20,48,49] Mg containing catalysts have showed long-term stability which has been attributed to low sintering of the nickel leading to reduced carbon formation.[33] For this reasons this kind of Mg modification might make a suitable catalyst for high temperature SR. A caveat exists where excessive Mg doping may cause a drop in hydrogen activity.[47]

Co modification

Based on what has been presented in previous work, a Co modification should lead to better control of undesired reactions that occur on the Ni metal especially at lower reforming temperatures.[41] As presented on Table 8, The unsupported NiCo being a bulk material is presented as 100% loading while the supported NiCo had a total metal loading of about 17% with far superior dispersion. The unsupported NiCo catalyst has a large portion of the metals as structure leaving a small portion of exposed metal relative to the amount of metal as validated by the lower dispersion.

The metal dispersion for the Ni/Al (shown above) appeared higher than the NiCo/Al albeit the total metal loading for the latter was higher. Since Co metal is also active for H₂ chemisorption, this could be a result of relatively larger metal crystallites.

Table 8. Co modified catalyst characterization by N₂ physisorption (BET S.A.) and H₂ chemisorption

Catalyst	Total metal loading (wt%)	Surface Area (m ² /g)	Active Surface Area (m ² /g cat)	Metal dispersion (%)
NiCo (1:4)	100	62	0.010	0.002
NiCo/Al	17.2	39	0.250	0.215

XRD analysis of the reduced NiCo catalysts are presented on Figure 26, including a comparison with the Ni/Al catalyst. On these Co containing catalysts, pure metallic Ni and Co phases were detected as well as an Al₂O₃ phase for the supported catalysts. Strong peaks were detected corresponding a NiCo₂O₄ spinel phase

The reaction tests for the Co containing catalysts at 460°C (Table 9 and Figure 27a) showed that the supported NiCo catalyst generated overall more coke but with a larger increase in hydrogen production as seen by the coke selectivity measurement..

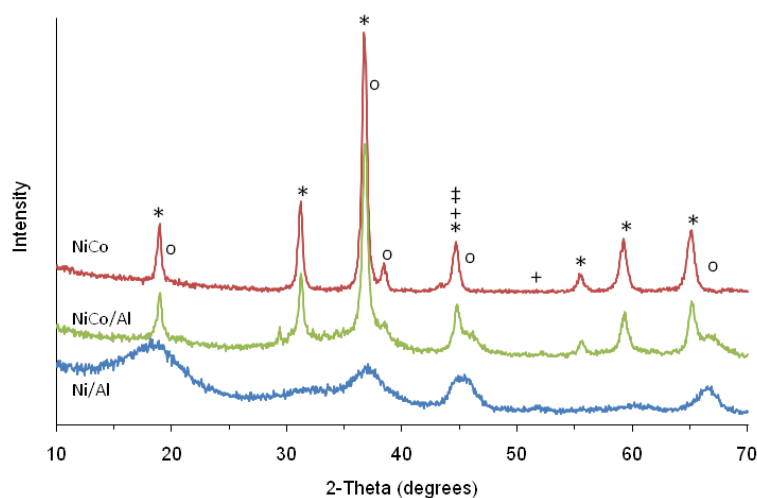


Figure 26. XRD analysis of the reduced Ni-Co catalysts compared to the Ni/Al: Ni (+), NiCo₂O₄ (*), Al₂O₃ (o), Co (‡)

This reduction in selectivity to coke for the supported NiCo catalyst may correspond to a coking inhibition as this low reaction temperature is insufficient for coke removal during SR.

The results for the unsupported catalyst were not necessarily different from those of the Ni catalyst. However, an interesting difference was observed between the results for the supported and unsupported NiCo catalysts. These results seem to support the idea the Al₂O₃ not only serves to increase dispersion but that it plays an important role in the selectivity of the SR reaction.

Table 9. SR reaction testing results for Co modification tests; S/C=6, mass balance 98±3%

catalyst	Ni/Al	NiCo	NiCo/Al ^a	Ni/Al	NiCo	NiCo/Al ^a
T (°C)	460	460	460	650	650	650
Conversion (mol%)	0.17	0.81	0.69	0.65	0.48	0.79
H ₂ (mol/hr)	0.55	4.50	4.07	4.48	1.57	5.53
CO ₂ (mol/hr)	0.28	1.99	2.07	2.16	0.49	2.65
CO (mol/hr)	0.09	0.53	0.19	0.36	0.94	0.52
CH ₄ (mol/hr)	0.02	0.02	0.02	0.10	0.18	0.13
^b C _S (mol/hr) * 10 ³	0.8	6.5	4.07	1.0	0.9	1.71
H ₂ ^{stoich} yield (mol%)	6.5	53.2	48.1	52.9	18.6	65.3
^b C _S mol/H ₂ mol	0.147	0.143	0.10	0.022	0.059	0.03

^a these values represent averages from replicate

^b C_S refers to carbon from coke deposits

The results also suggest that these three species may be acting synergistically to improve the hydrogen productivity over coke forming reactions. In terms of gas product selectivity there was no clear difference between all three catalysts at 460°C such that these comments are made on the basis of hydrogen and coking.

It was also found that at 460°C, the bimetallic catalysts seemed to have superior conversion of acetic acid despite their lower BET surface area and even dispersion when compared to the Ni/Al catalyst. The modification of the metallic phase may have a stronger effect than the effect of the support and metal dispersion as tested for this report.

From this set of tests it is unclear if a reduction in coke selectivity corresponds to a reduction in the ketonization reaction. However it must be noted that acetone formation was detected especially for the NiCo catalysts suggesting that the formed ketone might not activate to generate coke precursors as readily as it may on a Ni/Al catalyst. This observation seems to support that a Co modification of a Ni catalyst may tune the C-C bond cleavage rate to decrease the rate of polymerization reactions of fragments or even from ketone product but only at a low temperature regime.

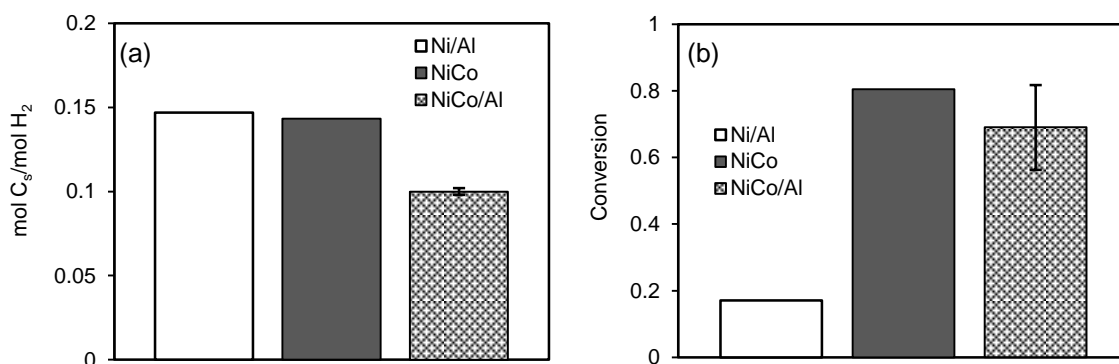


Figure 27. a)Coke as function of hydrogen generation for NiCo catalysts compared to the Ni/Al, b) acetic acid conversion; 460°C, S/C=6

Both bimetallic catalysts tested at the higher SR temperature (Figure 28) showed an apparent increase in coke selectivity when compared to the supported Ni catalyst. At 650°C the Ni/Al catalyst seemed to generate the lowest coke per mole of hydrogen with a similar gas product

profile. The supported NiCo catalyst seemed to favor hydrogen production as opposed to coke when compared to the unsupported NiCo catalyst. These results seem to suggest that the Co modification may play a different role at the elevated temperature that it does at the lower temperature regime for acetic acid SR. One possibility could be that the rate of C-C cleavage at this elevated temperature is actually increased for the Co or the spinel. It must also be noted that neither the Co nor the resulting bimetallic catalyst are known for promoting gasification reactions so that the coking effect may be different to what results from Mg modification of the support.

At 650°C with conversions above 50% the coke generated corresponded to well below 1% of the mass balance for all catalysts tested. One must be careful while interpreting what this result means. A coking extent of around 1% of the mass balance can still be enough to affect the hydrogen yield, block catalyst pores leading to reactor plugging, and deactivate the catalyst.

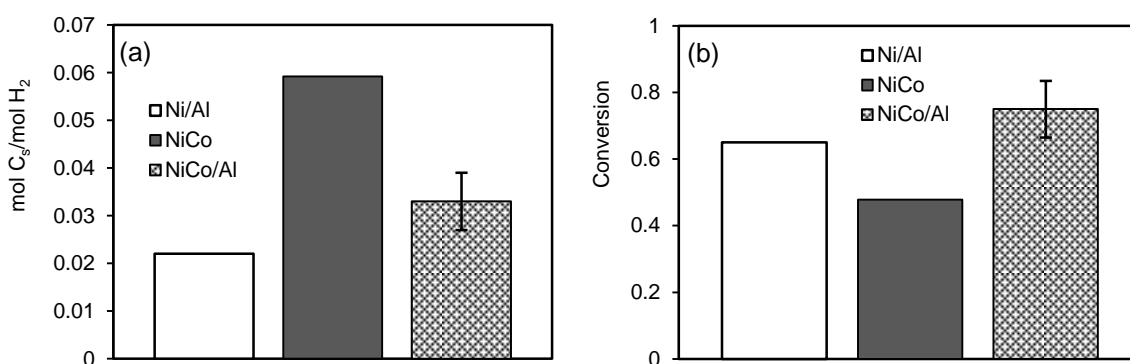


Figure 28. a)Coke as function of hydrogen generation for NiCo catalysts compared to the Ni/Al, b) acetic acid conversion; 650°C, S/C=6

From the catalysts tested, a supported bimetallic NiCo catalyst is desired to minimize coke formation at the low SR temperature while keeping a high level of activity and hydrogen production from acetic acid. The role of the support and metal dispersion seemed vital to be able to achieve improvements with the bimetallic catalyst.

This work may serve as a basis for further screening of Co modified catalysts for acetic acid SR as a highly coking light bio-oil species. It must be noted that the Ni:Co ratio used was based on disappearance of acetic acid and gas product selectivity and not necessarily for coke minimization.[41] From the results presented, a NiCo/Al with higher BET surface area could be an interesting catalyst to test for reduced temperature SR since a high surface area Al_2O_3 may be beneficial as shown the data for the Mg modification tests suggested. Other bio-oil species should be tested with this type of catalyst to validate the results herein.

Conclusions

Two SR temperature regimes have been defined to study different rates of coke accumulation from acetic acid. 650°C was defined as a high SR temperature where coke removal by steam is favored. A lower SR temperature like 460°C may show kinetically favored coke formation without significant coke removal by steam. The use of a mixed Mg and Al support for reforming catalyst may help control net coke accumulation at the higher temperature but likely make a less active catalyst at the low SR temperature. The effect of support needs to be studied further since it did show some trend with catalyst structure and porosity (based on BET) especially at the low temperature. Ni/Mg/Al catalysts may be suitable for SR of bio-oil species at elevated temperatures.

A supported NiCo bimetallic catalyst showed moderate improvement in coke selectivity while preserving hydrogen productivity at 460°C . This result suggested that coke generation was not favored since this temperature was shown insufficient to activate the coke with steam. This type of bimetallic catalyst seems like a viable choice for SR at reduced temperatures. Co addition was not necessarily favorable for coke reduction at the higher temperatures where catalytic properties actually seem to favor coke formation.

An important role was found for the Al_2O_3 support in the case of the bimetallic catalyst where coke selectivity appeared to be consistently lower than the case of the unsupported catalyst. It becomes interesting to further explore tuning the catalytic properties and even structure of the reforming catalyst at the low temperature regime for oxygenated or bio-oil reforming.

Acknowledgement. This paper was prepared with the support of the Bioeconomy Institute (Iowa State University).

References

1. Wang D, Montane D, Chornet E: Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde. *Applied Catalysis a-General* 143(2), 245-270 (1996).
2. Hu X, Lu G: Investigation of the steam reforming of a series of model compounds derived from bio-oil for hydrogen production. *Applied Catalysis B: Environmental* 88(3-4), 376-385 (2009).
3. Wang D, Czernik S, Montane D, Mann M, Chornet E: Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. *Industrial & Engineering Chemistry Research* 36(5), 1507-1518 (1997).
4. Galdamez JR, Garcia L, Bilbao R: Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni-Al Catalysts. Acetic Acid as a Model Compound. *Energy Fuels* 19(3), 1133-1142 (2005).
5. Takanabe K, Aika K-I, Seshan K, Lefferts L: Sustainable hydrogen from bio-oil-- Steam reforming of acetic acid as a model oxygenate. *Journal of Catalysis* 227(1), 101-108 (2004).
6. Jung S-H, Kang B-S, Kim J-S: Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *Journal of Analytical and Applied Pyrolysis* 82(2), 240-247 (2008).
7. *Deactivation and Regeneration*. In: *Studies in Surface Science and Catalysis*, Tanabe K, Misono M, Ono Y, Hattori H. Elsevier, 339-346 (1989).
8. Takanabe K, Aika K-I, Inazu K, Baba T, Seshan K, Lefferts L: Steam reforming of acetic acid as a biomass derived oxygenate: Bifunctional pathway for hydrogen formation over Pt/ZrO₂ catalysts. *Journal of Catalysis* 243(2), 263-269 (2006).
9. *Definition and Classification of Solid Acids and Bases*. In: *Studies in Surface Science and Catalysis*, Tanabe K, Misono M, Ono Y, Hattori H. Elsevier, 1-3 (1989).
10. Sie S, Sie: Acid-catalyzed cracking of paraffinic hydrocarbons. 2. Evidence for the protonated cyclopropane mechanism from catalytic cracking experiments. *Industrial & engineering chemistry research* 32(3), 397 (1993).
11. Hattori H: Heterogeneous Basic Catalysis. *Chemical reviews* 95(3), 537 (1995).
12. Matsuoka K: Steam Reforming of Woody Biomass in a Fluidized Bed of Iron Oxide-Impregnated Porous Alumina. *Energy & Fuels* 20(6), 2727 (2006).
13. Bernardo C, Bernardo: The kinetics of gasification of carbon deposited on nickel catalysts. *Carbon* 17(2), 115 (1979).
14. Trimm D: Catalysts for the control of coking during steam reforming. *Catalysis Today* 49(1-3), 3 (1999).
15. Davda R, Davda: A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts. *Applied catalysis. B, Environmental* 56(1-2), 171 (2005).

16. Kechagiopoulos P., E. Vagia, A. Iordanidis, S. S. Voutetakis, A.A. Lemonidou, Vasalos IA: Hydrogen production from renewable energy sources: reforming of biogas and bio-oil. *Catalysis, Energy and Environment. Workshop of CPERI*, (2004).
17. Rostrup-Nielsen JR: Coking on nickel catalysts for steam reforming of hydrocarbons. *Journal of Catalysis* 33(2), 184-201 (1974).
18. Czernik S, French R, Feik C, Chornet E: Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Industrial & Engineering Chemistry Research* 41(17), 4209-4215 (2002).
19. Galdámez JR, García L, Bilbao R: Hydrogen Production by Steam Reforming of Bio-Oil Using Coprecipitated Ni–Al Catalysts. Acetic Acid as a Model Compound. *Energy & Fuels* 19(3), 1133-1142 (2005).
20. Garcia L, French R, Czernik S, Chornet E: Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. *Applied Catalysis A: General* 201(2), 225-239 (2000).
21. Kechagiopoulos P.N., Voutetakis S., Lemonidou A., I AV: Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-oil in a Fixed Bed Reactor. *Energy and Fuels* (20), 2155-2163 (2006).
22. Markevich M, Czernik S, Chornet E, Montane D: Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil. *Energy Fuels* 13(6), 1160-1166 (1999).
23. Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R: Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. *Applied Catalysis B: Environmental* 61(1-2), 130-139 (2005).
24. Czernik S, Evans R, French R: Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catalysis Today. Recent Advances in Catalytic Production of Hydrogen from Renewable Sources* 129(3-4), 265-268 (2007).
25. Satrio JA, Shanks BH, Wheelock TD: Development of a novel combined catalyst and sorbent for hydrocarbon reforming. *Industrial & Engineering Chemistry Research* 44(11), 3901-3911 (2005).
26. Eggeman T: Ammonia. John Wiley & Sons, Inc., (2000).
27. Vizcaíno AJ, Carrero A, Calles JA: Hydrogen production by ethanol steam reforming over Cu-Ni supported catalysts. *International Journal of Hydrogen Energy* 32(10-11), 1450-1461 (2007).
28. Vizcaíno AJ, Arena P, Baronetti G *et al.*: Ethanol steam reforming on Ni/Al₂O₃ catalysts: Effect of Mg addition. *International Journal of Hydrogen Energy* 33(13), 3489-3492 (2008).
29. Frusteri F, Freni S, Chiodo V *et al.*: Steam reforming of bio-ethanol on alkali-doped Ni/MgO catalysts: hydrogen production for MC fuel cell. *Applied Catalysis A: General* 270(1-2), 1-7 (2004).
30. Lisboa JDS, Santos DCRM, Passos FB, Noronha FB: Influence of the addition of promoters to steam reforming catalysts. *Catalysis Today* 101(1), 15-21 (2005).
31. Cavallaro S, Mondello N, Freni S: Hydrogen produced from ethanol for internal reforming molten carbonate fuel cell. *Journal of Power Sources* 102(1-2), 198-204 (2001).

32. Basagiannis AC, Verykios XE: Catalytic steam reforming of acetic acid for hydrogen production. *International Journal of Hydrogen Energy* 32(15), 3343-3355 (2007).
33. Guo J, Lou H, Zhao H, Chai D, Zheng X: Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. *Applied Catalysis A: General* 273(1-2), 75-82 (2004).
34. Koo KY, Roh H-S, Jung UH, Seo DJ, Seo Y-S, Yoon WL: Combined H₂O and CO₂ reforming of CH₄ over nano-sized Ni/MgO-Al₂O₃ catalysts for synthesis gas production for gas to liquid (GTL): Effect of Mg/Al mixed ratio on coke formation. *Catalysis Today* 146(1-2), 166-171 (2009).
35. Choudhary VR, Uphade BS, Mamman AS: Oxidative Conversion of Methane to Syngas over Nickel Supported on Commercial Low Surface Area Porous Catalyst Carriers Precoated with Alkaline and Rare Earth Oxides. *Journal of Catalysis* 172(2), 281-293 (1997).
36. Sutton D, Kelleher B, Ross JRH: Review of literature on catalysts for biomass gasification. *Fuel Processing Technology* 73(3), 155-173 (2001).
37. Busca G, Costantino U, Montanari T, Ramis G, Resini C, Sisani M: Nickel versus cobalt catalysts for hydrogen production by ethanol steam reforming: Ni-Co-Zn-Al catalysts from hydrotalcite-like precursors. *International Journal of Hydrogen Energy* 35(11), 5356-5366 (2010).
38. Hardiman K, Hardiman: Performance of a Co-Ni catalyst for propane reforming under low steam-to-carbon ratios. *Chemical engineering journal* 102(2), 119 (2004).
39. Hardiman K: Multivariate Analysis of the Role of Preparation Conditions on the Intrinsic Properties of a Co-Ni/Al₂O₃ Steam-Reforming Catalyst. *Industrial & engineering chemistry research* 43(19), 6006 (2004).
40. Zhang J, Wang H, Dalai AK: Development of stable bimetallic catalysts for carbon dioxide reforming of methane. *Journal of Catalysis* 249(2), 300-310 (2007).
41. Hu X, Lu G: Investigation of steam reforming of acetic acid to hydrogen over Ni-Co metal catalyst. *Journal of Molecular Catalysis A: Chemical* 261(1), 43-48 (2007).
42. Mccarty JG, Wise H: Hydrogenation of surface carbon on alumina-supported nickel. *Journal of Catalysis* 57(3), 406-416 (1979).
43. Sánchez-Sánchez MC, Navarro RM, Fierro JLG: Ethanol steam reforming over Ni/M_xO_y-Al₂O₃ (M=Ce, La, Zr and Mg) catalysts: Influence of support on the hydrogen production. *International Journal of Hydrogen Energy* 32(10-11), 1462-1471
44. Coleman LJI, Epling W, Hudgins RR, Croiset E: Ni/Mg-Al mixed oxide catalyst for the steam reforming of ethanol. *Applied Catalysis A: General* 363(1-2), 52-63 (2009).
45. Tian L, Zhao XH, Liu BS, Zhang WD: Preparation of an Industrial Ni-Based Catalyst and Investigation on CH₄/CO₂ Reforming to Syngas. *Energy & Fuels* 23(2), 607-612 (2009).
46. Frusteri F, Frusteri: Steam reforming of bio-ethanol on alkali-doped Ni/MgO catalysts: hydrogen production for MC fuel cell. *Applied catalysis. A, General* 270(1-2), 1 (2004).
47. Yang J, Sun Y, Tang Y *et al.*: Effect of magnesium promoter on iron-based catalyst for Fischer-Tropsch synthesis. *Journal of Molecular Catalysis A: Chemical* 245(1-2), 26-36 (2006).

48. *Catalysis*. Ross JRH. The Royal Society of Chemistry, London (1985).
49. Wang S, Lu GQM: CO₂ reforming of methane on Ni catalysts: Effects of the support phase and preparation technique. *Applied Catalysis B: Environmental* 16(3), 269-277 (1998).

Chapter 6. General Conclusions

Hydrogen can be produced from steam reforming of water-soluble bio-oils. The water-soluble bio-oil could be extracted from whole bio-oil or obtained from fractionated bio-oil. Bio-oil fractions can be obtained from special collection systems and steam reformed to gain insight on the effect of bio-oil composition. A light fraction characterized by the presence of acetic acid and acetol was found to be more suitable for steam reforming when compared to fractions with higher portions of higher molecular weight species and carbohydrates.

A model compound study was performed to study the reactivity and tendency towards carbon deposition of different types of species representing some of the most abundant water-soluble species in bio-oils. The experiments were performed aiming towards kinetic control to better study reaction characteristics in contrast with previous studies. The work at low conversions and kinetic regime helped on deconvoluting the contributions of thermodynamic and transport control from the reaction characteristics. This is a fundamental difference in this work when compared to previous published work on model compound steam reforming studies.

Reaction kinetics and selectivity (desired products vs. undesired products) are strongly dependent on the type of catalyst employed, where thermodynamics are not. This way thermodynamics as well as diffusion resistance may mask the interaction between the feed molecule and the catalyst. The aim of this study was to study the interaction between the feed molecules and a Nickel-Alumina reforming catalyst. In order to study reaction characteristics of the model species over the reforming catalyst it is necessary to work under carefully controlled conditions defined as a kinetic control regime or absence of thermodynamic and diffusion limitations.

This study revealed that acetic acid, furfural and levoglucosan were the most troublesome species for steam reforming. Levoglucosan tended to thermally decompose to carbon deposits even in the absence of a catalyst. Acetic acid and furfural were more thermally stable than the carbohydrate but were the most selective to coke over the reforming catalyst. Acetic acid is typically the most abundant species in water-soluble bio-oils as well as in

light-end bio-oil fractions thus it is a key molecule to study in order to try to minimize coke deposition and promote hydrogen formation.

In order to study the effect of catalyst modifications it was also necessary to operate under kinetic controlled conditions as defined on the model compound study. Two different reforming catalyst modifications were proposed. Addition of Mg to the support of a Ni/Al₂O₃ reforming catalyst can result in an improvement in the net coke deposition at high temperatures which favor steam gasification of carbon. This behavior was attributed mostly to this carbon removal rather than minimization of coke formation as the Mg modified catalysts failed to show improvement at the lower temperatures.

A metal phase modification, of the supported catalyst, with Co resulting largely in the formation of a NiCo spinel led to improvement in coke deposition at the low reforming temperature. This effect was unique since it implies an improvement in hindering coke formation at the low temperature. Improvement from Co modification could be explained by a modification in the formation of surface carbides arising from C-C cleavage reactions on the metal. This property, similarly to that observed with hydrocarbon reforming, could be a key reaction in controlling coke formation from bio-oil oxygenates. This case is also supported by results from single carbon oxygenated species resulting in negligible amounts of coke. The behavior of the catalysts supported on alumina was generally superior to all other catalysts especially at the lower temperatures. Thus, the alumina appeared to be essential for hydrogen production relative to coke formation at these temperatures. Further research with acetic acid could unveil possibilities to minimize coking and maximizing hydrogen yields from carboxylic acid-rich bio-oils.

Future Directions

Some questions remain after this work that could be addressed with further analytical or experimental research. A next logical step could be to optimize NiCo bimetallic catalyst formulations for coke reduction at low reforming temperatures by utilizing acetic acid as a problem model species. An alternative approach could be to introduce different Ni metal

modifications to improve coke deposition at elevated temperature reforming where an Alumina-Magnesium support could be used to simultaneously promote gasification of the coke accumulated. An analytical study could also help identify specific reaction intermediates that promote coking. And ultimately it is clear that new developments in bio-oil separation and stabilization strategies will also help in trying to minimize coke deposition for more efficient hydrogen production.

In the case of low temperature reforming coking control, different formulations of NiCo bimetallic catalyst could be tested. The goal of this type of study would be to study, for example, different proportion of Ni to Co (i.e. 1:4, 1:2, 1:1, 2:1, etc.) to introduce different modifications that could reduce coke deposits while maximizing hydrogen production. One interesting formulation would be for example a 1:2 Ni to Co metal molar ratio which corresponds to the stoichiometry of the NiCo_2O_4 spinel identified in this work. This formulation could favor the formation of the spinel to study its effect independently from pure Ni or Co phases which could be related to the improvement on coke deposition at low temperature reforming of acetic acid. Evidently this insight would contribute to the knowledge of coking control of the complex water soluble bio-oils.

Another possibility is to work on the development of a catalyst that combines the benefits observed of coke control at low and high reforming temperatures. From this dissertation work it is clear that these types of catalyst modifications introduce an opportunity to control coke accumulation at two temperature regimes exclusively. There is no ground to expect improvement from a combination of the formulations tested at a particular temperature regime. A catalyst modification by proportion of Co or other metals with Ni could provide an opportunity to modify the coke generation at higher temperatures as well. Evidently the formulation tested herein did not have such an effect at elevated temperatures and thus the need to study different metal modifications to achieve balance between the formation of coke precursors and the desired products at elevated temperatures where a modified support could help promote coke removal.

On the fundamental level an aspect that could be studied further is the identification of surface species or intermediates and the effect of metal or support modifications on the

formation or disappearance of these. An example of this would be the stabilization and desorption of reaction intermediates that lead to coke formation.

Improvements in bio-oil fractionating systems could provide opportunities to obtain better control on the bio-oil composition which greatly influences upgrading reactions like steam reforming. The results from the model compound studies in the present work could serve as a guide in order to produce bio-oil with desirable properties. Improved bio-oil fractions have the potential to generate hydrogen with minimal coke formation. It is also sought that this type of fraction does not contain important amounts of the biomass minerals (ash) that could poison the reforming catalysts. This issue has been discussed in the past by proposing for example, biomass pretreatments to remove these amounts of ash that could strongly affect the product distribution in the bio-oils.

Appendix A. Initial Experimental Setups

Bio-oils cannot be vaporized because they tend to polymerize upon heating at temperatures about 80 °C and at higher temperatures they start to decompose. Experimentally, the inability of the pyrolytic lignin to be volatilized for reforming can lead to thermal cracking before ever reaching the catalyst. Difficulties found in re-volatilization of pyrolytic lignin led to the use of fractionated bio-oil where only the aqueous extract is used for reforming (Radlein et al. 1999). This phenomena leads to a solid cracking product, that would physically cover the catalytic surfaces and thus reducing the catalytic activity or effectiveness. The following descriptions correspond to the initial experimental setup corresponding to the steam reforming of bio-oil fractions.

Fixed bed bio-oil steam reformer

Design goals

One of the initial goals for the experimental set-up design was to provide good mixing of the reactants, i.e. bio-oil and water. The interest was on the water-soluble bio-oil fraction so the bio-oil and water could be premixed and co-fed to the reactor. The methods for preparation and characterization of the solutions will be discussed in a later section. Another goal of the design was to build an injector system that would provide atomization of the feedstock solutions. Czernik *et al.* successfully employed an ultrasound nozzle for low pressure drop and low flow rates of bio-oil. There was no other low cost similar scale atomization nozzle commercially available so a custom spray system was designed.

The spray system initially employed 1/16" o.d. stainless steel tubing for the injection of the feedstock and mixed in a "T" with the nitrogen gas. This way the nitrogen would bubble and force the liquid at a higher velocity and spray inside the reactor and over the catalyst.

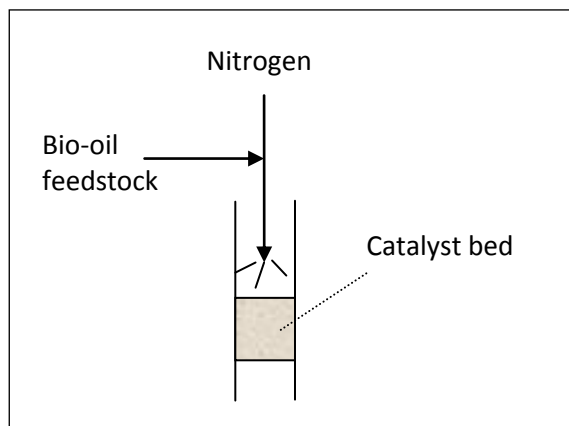


Figure A-1. Schematic drawing of bubble injection system

It was also intended for this configuration to inject the liquid feedstock inside the reactor and close to the bed surface for a quick initial contact with the catalyst. There were some limitations found with this technique and are discussed later.

Reactor setup overview (fractionated bio-oil)

A laboratory scale reactor was designed to be operated as a fixed bed catalytic reactor. The reactor consisted of a tubular quartz reactor with a ground quartz plate as catalyst bed support. The reactor was 42 cm long and had an internal diameter of 12.7 mm. The bed catalyst bed was supported by a ground quartz frit located above the center of the reactor so that the bed location was raised to minimize preheating of the freeboard zone.

The reactor was placed inside a vertical electric heater and both ends of the reactor were insulated with ceramic wool to minimize heat losses. A series of K-type thermocouples were placed to monitor the system temperatures. A thermocouple was located at the outer surface of the gas pre-heater tube. Another thermocouple was used to monitor the bed temperature. The location of this thermocouple is later explained. A couple other thermocouples were placed to monitor the heating coils of the furnace, and the cooling bath temperature. Both the reactor furnace and the heat tape power inputs were controlled in feedback loops by separate temperature controllers. The controllers were located on a custom built control box together with a selectable thermocouple display.

Nitrogen was used as inert carrier gas to insure proper flow properties and as an external standard to facilitate the quantification of the gas products. An Alicat MC series mass flow controller was used to keep an accurate and constant flow of nitrogen to the system. Hydrogen gas was used to activate the catalyst. Compressed air was also available for regenerating the catalyst by gasification of carbon deposits. A panel of set of valves and switches was used to control which gases would be entering the reactor. A gas preheating section was located right before the connection to the reactor top. This section was heated by using a variable current heat tape. This was mainly used to slightly pre-heat the nitrogen flow and help minimize overall heat losses.

The reactor was loaded with about 5 g of steam reforming catalyst (for maximum conversion experiments). The catalyst was mixed with 1 to 3 g of crushed low surface area silicon carbide pellets (2 mm size) to improve heat transfer and increase bed height. The overall bed height was about three times the bed diameter. This insured the proper flow across the bed avoiding channeling.

A 25 mL gas condenser made of pyrex filled with water was placed bellow the reactor. The gas stream exiting the reactor was passed into the condenser where it bubbled through the water condensing excess water and any unreacted feedstock. The condenser was cooled by placing it inside an ice-salt-water bath. The salt was a feed salt mixture that was cheaply acquired. The salt addition was initially determined to be close to 10% compared to the amount of ice used to obtain a low enough temperature to the catch light organics and water but avoiding freezing of the liquid inside the condenser. A second dry impinging condenser was added to collect any excess moisture. Then a Drierite® loaded moisture trap was used to remove any remaining moisture.

The liquid feedstock was accurately injected by a single infusion KD Scientific programmable infusion pump located above the reactor. The nitrogen mass flow controller was also used to continuously monitor the upstream absolute pressure of the system. A pressure gauge was used to monitor the downstream pressure of the reactor. This way the pressure drop across the bed could be monitored as well as helping identify possible leaks. A pressure maintaining relief valve was placed after the pressure gauge to set the operating

pressure in case the product gas analysis unit would not be available. This pressure valve also served as a tool to make sure there were no leaks and that all the reactants and gas flow properly through the reactor.

Reactor design issues

The quartz reactor configuration was advantageous because it provided the opportunity to setup and start-up accurately and consistently. The careful placement of the reactor thermocouple and the accurate position of the injection system proved vital to get good results. Qualitative analysis of the catalyst bed and carbon deposition inside the reactor was facilitated also. The nature of the quartz-quartz, quartz-metal fittings made the system also susceptible for leaks. Vacuum grease and a series of clamps were used to minimize these issues. The reactor system in turn had to be supervised at all times to insure that all leaks were quickly identified and fixed.

Bed thermocouple location

Following previous work the reactor temperature readings were taken from a thermocouple placed below the catalyst support indirectly measuring the catalyst temperature. The system designed to hold a thermocouple from the bottom of the reactor forced having the reactor outlet above the thermocouple entrance, this way there was a stagnation point for liquids to collect. A thermocouple was then placed inside and in close contact with catalyst bed from the top opening of the reactor. A short study was performed to determine difference in readings of both thermocouples compared to the actual heater temperature. The results are included in the appendix. This simple test showed that with this setup the temperature observed below the bed support tends to be lower than the actual bed temperature in some cases the difference was about 40°C.

Several issues were found as the nitrogen feed line, the liquid feed tubing and the thermocouple should all be entering through the top of the reactor. The liquid feed line had to reach inside the reactor and so the thermocouple so a high temperature rubber septum was

used to fit both lines straight into the reactor. This setup for the reactor inlet was favored due to ease of maintenance and because all its parts were easily replaceable.

Initial testing

Acetic acid and water solutions were originally selected to model bio-oil as commonly done in the literature to set up the reactor and help design the experimental and analytical methods. Acetic acid was mixed with excess water to a S/C molar ratio of 6. This ratio represents an excess of water and this way a complete steam reforming plus water-gas shift is obtained. The acetic acid solutions were introduced into the reactor which was heated to 550°C using the bubble nozzle at a liquid feed between 4-20 mL/hr and a N₂ flow rate of 200 ccm, both ratios high enough to provide constant injection to the reactor.

A particular limitation was found when using the bubble injection system. During acetic acid SR the concentration of desired hydrogen and carbon dioxide quickly decreased showing either reactor blockage or rapid catalyst deactivation (Figure A-2). After a 60 min run the reactor walls were visibly covered with carbon where the bed was located and the headspace around the injection point. This deposition suggests severe thermal decomposition of the acetic acid over the hot reactor walls and also severe coking over the catalyst surface.

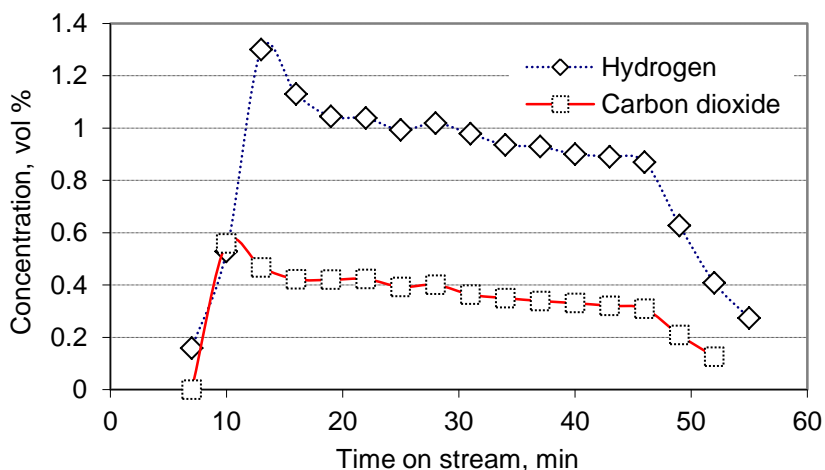


Figure A-2. Example of product concentration profile of acetic acid reforming (S/C=6, W = 0.1g)

It was observed that the furnace used did not provide even heat in the axial direction. Visibly the hottest region was found to be the upper center region. Now in order to minimize the preheating or cracking section the reactor configuration was such to place the bottom of the bed right above the hottest region, e.g. by flipping the reactor upside down. Also the bubbling injection system was found to spray significant amount of the feedstock directly over the hot reactor walls and thus promoting thermal decomposition reactions.

Further runs were performed to try to correct these issues but persistent limitations led to later use a more stable model compound like methanol. Methanol was selected being the simplest bio-oil oxygenated model compound. It is known that methanol is much more thermally stable than acetic-acid and would serve better for equipment shakedown tests and mass balances. The purpose of these mass balances was to refine the proposed experimental and analytical methods.

Methanol steam reforming was performed at similar molar feed flow rates in analogy to methane steam reforming as presented in Satrio *et al.* For methanol reforming there was no carbon deposition observed in any of the runs and the conversions were up to 85 mol% even when using very little amount of catalyst. The system pressure was found that needed to be at least 1 psig to facilitate gas analysis, this way a pressure of 5.0 psig was selected for all further runs to facilitate flow of gas through the bed and help identify leaks.

The limits of the process parameters were found to be 20 mL/hr liquid feed, stable temperatures up to 800°C, amount of catalyst up to 4-10 g, condensate collection volume up to 25 mL, N₂ flow rates higher than 200 mL/min, and system pressure of about 6 psi.

Initial bio-oil reforming issues

As the first samples of bio-oil were run for initial testing in the steam reformer several issues were found related with their thermal instability. The liquid feed tube was located close above the hot catalyst surface so that simultaneous vaporization and reaction would occur to reduce residence time and avoid thermal decomposition effects. This setup utilizes an approach similar to the flash catalytic volatilization discussed in the work by Salge *et al.* This

setup reduced the visible carbon deposits occurring on the quartz surface but this tubing would receive direct radiation from the electric furnace. This injector tube was also difficult to keep centered inside the reactor to avoid direct contact with the reactor walls. In many tests the tubing quickly clogged with solid deposits so that it was later designed to drop the bio-oil solutions from a region above the heating elements and bent so that it would consistently inject at a similar distance from the reactor walls. This setup minimizes preheating by dropping the cool feedstock from out of the heating regions of the reactor directly over the hot catalyst section.

In an attempt to collect all the possible condensates to be able to determine overall conversion of the bio-oil feedstock the temperature of the ice bath was reduced by adding an amount of salt. This caused in many cases that the liquid catch in the condenser to freeze. Whenever this happened it impeded the gases to come out of the reactor and thus the upstream pressure was increased while the downstream pressure dropped. It was found that adding just about 2 g of salt was enough to eventually achieve a temperature close to -4°C . This was enough to catch most of the condensates which for most of the runs only water was detected.

Reactor modifications

A thermocouple was placed inside the catalyst bed inserted through a septum at the top of the reactor to measure directly the bed temperature. This way a stagnation point for condensates was also eliminated. A plastic syringe was connected to a lure-lok fitted 1/16" O.D. stainless steel tube inserted through a septum and inside the reactor to inject by dropping the liquids on top of the hot catalyst bed from outside the heating regions. The nitrogen pre-heater was set to slightly pre-heat the carrier gas at about 80°C which showed to help improve the isothermal characteristics during reaction runs.

Steam reforming of acetic acid ($\text{S/C}=6$) was performed again to test the new reactor setup and the experimental methods. It can be seen in Figure A-3 that a steady operation was achieved in about 10 minutes yielding mostly hydrogen and carbon dioxide at $T=500^{\circ}\text{C}$.

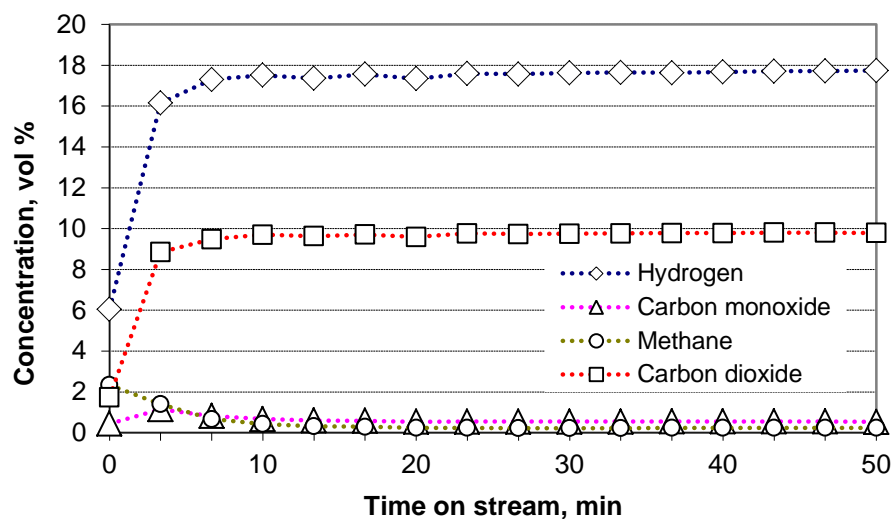


Figure A-3. Product concentration profile of acetic acid reforming after modifications (S/C=6, T=500°C, W=4.72g)

GCMS analysis

In this case there was no visible carbon deposited on the reactor walls like observed previously with the large preheating section and bubble injection. Also the excess of catalyst used seems to provide a more stable operation that permits the study of a steady production of hydrogen at higher conversions.

Table A-1 Table of retention times of the calibrated compounds for GCMS method used

Compound	RT (min)
Acetone	1.27
Acetic acid	1.65
2-methyl furan	1.75
acetol	2.23
2,4-pentane dione	4.31
furfural	5.74
furfuryl alcohol	6.64
3-furan methanol	7.11
5-methyl furfural	9.99
2-hydroxy-3-methyl-2-cyclopenten-1-one	12.1
levoglucosenone	14.3
5-(hydroxymethyl)-2-furancarboxaldehyde	18.2

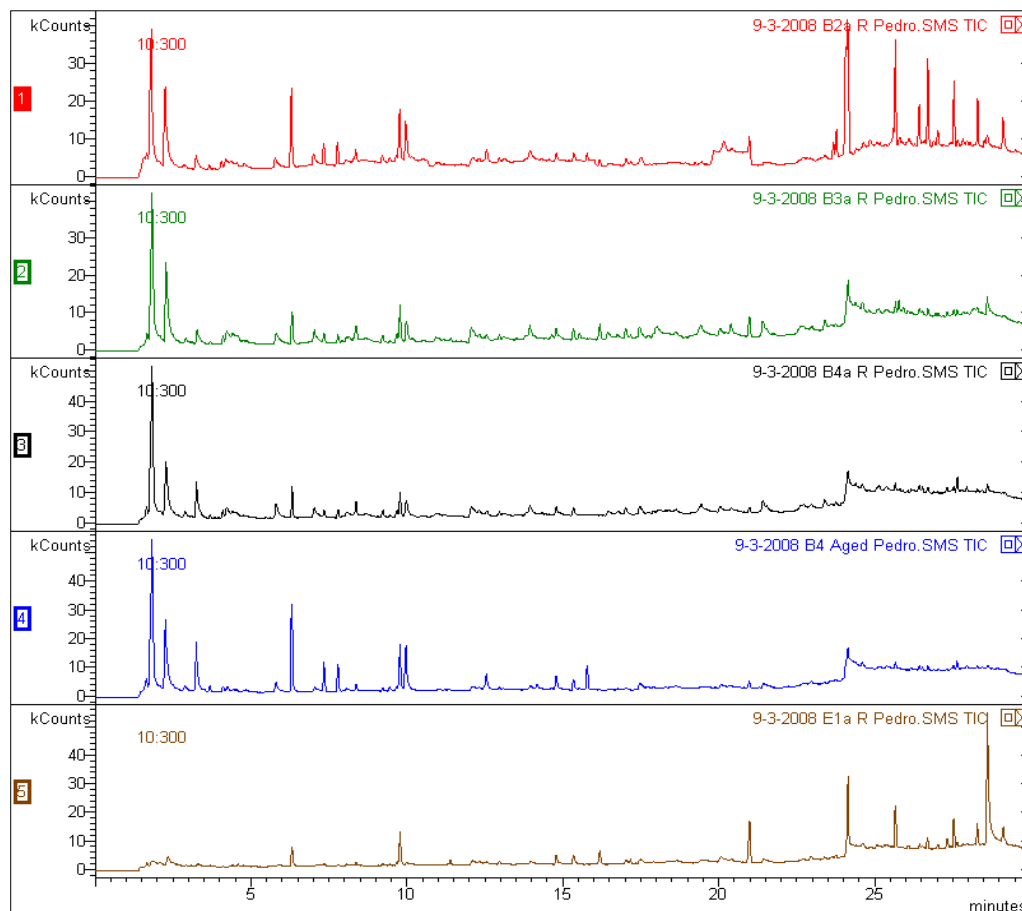


Figure A-4. Example of chromatograms from generated from GCMS analysis of aqueous bio-oil samples; B2-B4 correspond to cond. 2-4 samples, E1 sample corresponds to ESP sample.

Appendix B. Bio-oil and Catalyst Stability: Additional Observations

Bio-oil Stability

During initial experiments the aqueous samples that were stored for future tests eventually showed some noticeable changes. The solutions appeared cloudy, darker, and with visible suspended solids or flakes. Potentially important changes occur during storage of bio-oils especially being an unstable complex mixture that is acidic and has high water content. KF tests showed a decrease in the water content upon storage. The full bio-oil samples were also re-tested for KF and in this case it was basically unchanged. As reported in the literature the aqueous solutions containing high water content and the acidity from the bio-oil tend to be more unstable than the full bio-oil. The reason why the water content of the aqueous samples would decrease is not well understood. For this work it is relevant to study the stability of these bio-oil solutions and its importance for steam reforming. The particular effect of aqueous bio-oil was studied by comparing fresh and aged solutions. The aging of the solution was studied in terms of steam reforming hydrogen yields, speciation, homogeneity and moisture content.

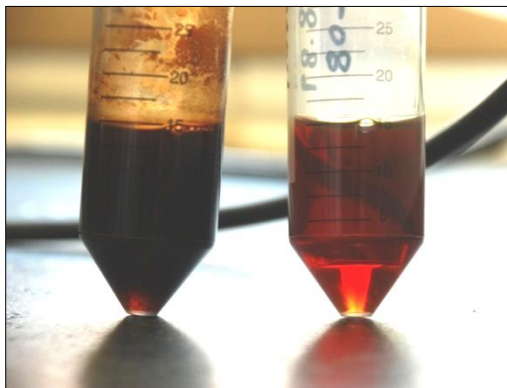


Figure B-1. Example of aged and fresh solution (condenser 2 sample about 90 days old, and a condenser 2 freshly prepared solution)

Some further experiments were performed to study in short effect of the visible particulates formed and suspended material in the reforming. A stored aqueous bio-oil sample was compared in terms of steam reforming with the presence of the particulates and after

filtration to remove these deposits. After filtration the solution seemed somehow clear again with a dark amber color. After reforming of both samples the results were very similar in terms of hydrogen yields and carbon conversion, both within the standard deviation. From this there is no clear difference provided by the presence of particulates and solids upon aging of the bio-oils.

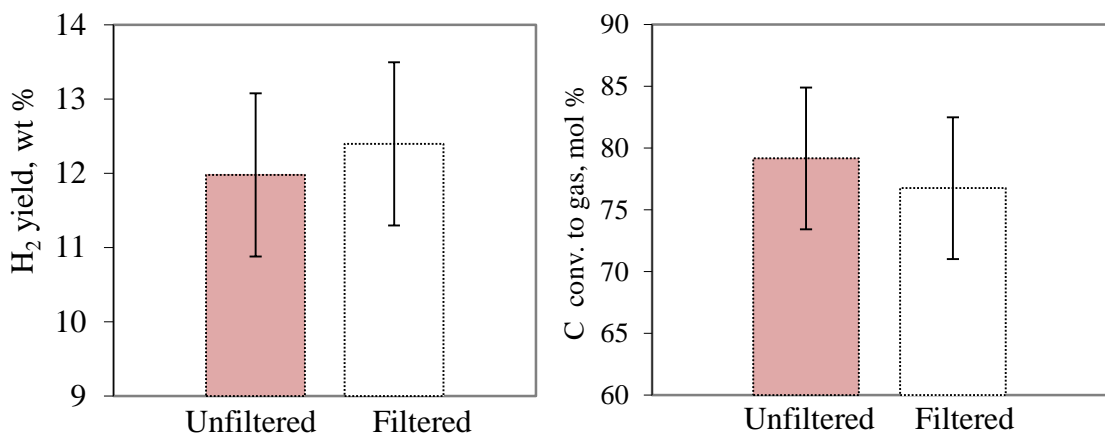


Figure B-2. Hydrogen yield of aged bio-oil solution before and after filtration (left), carbon conversion before and after filtration (right)

As discussed previously the commercial catalyst showed a decreased activity after a few hours-on-stream. It was observed that after removing the carbon deposits and treating with hydrogen the catalyst would not regain its initial activity. There are two main scenarios that could explain this behavior. The first is poisoning because of the possible presence of impurities that could adsorb irreversibly at the temperatures used. The second possibility is sintering, possibly because of extreme metal temperatures during carbon burn-off.

Catalyst Stability

H₂ chemisorption tests showed a decrease in metal surface that could be related to either case sintering by agglomeration of metal or surface deactivated by poisoning. X-ray fluorescence tests were later performed to detect contaminants as low as ppm level that could have

accumulated on the surface. Interestingly enough an increase in sulfur concentration was evident together with some chlorine and phosphorous, all known nickel catalyst poisons. It is important to point that there was no sulfur detected in any of the bio-oil solutions but even in a much lower concentration compared to the level of detection can have a cumulative effect on a the catalyst.

Table B-1 Hydrogen chemisorption analysis for fresh and deactivated catalyst

	Fresh	Used*
Dispersion at 11% loading (wt%)	4.19	1.28
Metallic surface area (m ² /g)	3.07	0.94

*oxidized

Table B-2 XRF analysis of fresh and deactivated catalyst

	S net kcps	SO ₃ Concentration, %	S wt %
Fresh cat.	0.122	0.008	0.003
Used cat.	1.101	0.070	0.028

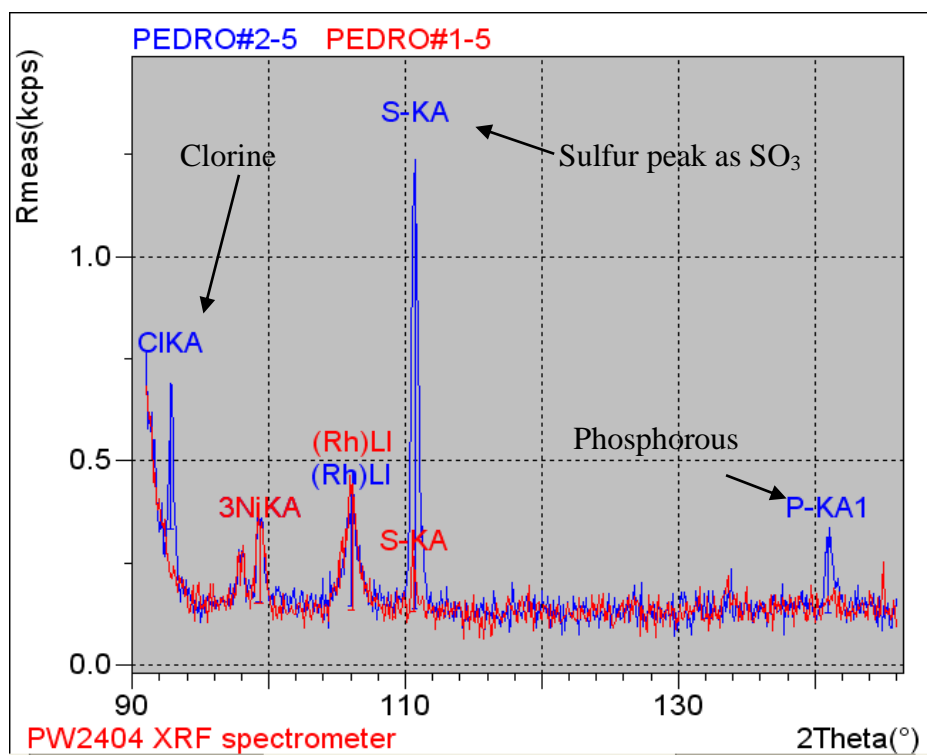


Figure B-3. XRF overlaid spectra; fresh catalyst (#1), used catalyst (#2)

Appendix C. Evaluation of a Bimetallic NiCo at High Conversion

Introduction

Recent investigations have employed an unsupported NiCo bimetallic catalyst for low temperature steam reforming (SR) of acetic acid as a biomass derived molecule. [1] Reaction testing results showed that a bimetallic catalyst with Ni:Co ion ratio of 1:4 was capable of activating the acetic acid and produce hydrogen with low methane and CO formation. Conditions tested included a low space velocity, providing a complete conversion by using an excess of catalyst, a S/C=7.5 and 400°C. A disadvantage of testing under these conditions is that at a high conversion there may be an effect as thermodynamic equilibrium is approached but also that there is no precedent to be able to compare these results with more traditional reforming catalysts. These conditions generated coke and acetone to less than 1% of the mass balance.

A question arises to whether this bimetallic catalyst particularly suppresses ketone and coke formation. To try to address this question, this same type of catalyst was tested against a Ni/Al (Ni/Al₂O₃) and a NiCo/Al at similar conditions to what reported. The objective was to compare in terms of actual extent of coking to a baseline Ni/Al catalyst (known for generating coke during SR of acetic acid) and a supported bimetallic catalyst.

In general terms, S/C ratios above 6 are considered an exceedingly high amount of water which may bring vaporization issues in the laboratory scale and cost issues at a larger scale. It is still important to try to validate the results from the literature where coke was found in less than 1% from the mass balance.

These tests compared the unsupported NiCo catalyst with a supported NiCo/Al and a supported Ni catalyst. Both high conversion (low space velocity) and low conversion (high space velocity) tests were performed. The results could be compared to the results under kinetic controlled conditions and ultimately to the results at the two temperatures defined for the coking study as in Chapter 4.

Experimental

The experimental set up and analytical aspects corresponded to what described on Chapter 4. Sample preparation corresponded to an acetic acid concentration giving a S/C of 7.5 while the temperature was kept at 400C.[1] Steady-state generation of hydrogen was recorded and total amount of accumulated carbon by Air-TPO.

High conversion experiments were performed at a low LHSV of 5 hr^{-1} , similar to what presented in the literature report where complete conversions were achieved for the unsupported bimetallic catalyst. Care must be taken while interpreting these high conversion results as they were performed under conditions of thermodynamic equilibrium and may not necessarily show the reaction kinetic behavior.

Low conversion tests were also performed to show kinetic products ($\text{LHSV}=120 \text{ hr}^{-1}$) at this particular set of conditions. These results will provide clues to what is the kinetic behavior of the NiCo catalyst while showing the implementation of this bimetallic strategy to a supported catalyst formulation.

Results and discussion

Figure C- represents the extent of coking relative to the hydrogen productivity as a measurement of coke selectivity at low space velocity. This calculation is important in trying to deconvolute effects of diminished activity from actual coking control. For these tests at complete conversion it can be observed that the Ni/Al catalyst had a tendency to generate more coke than the Co modified catalysts.

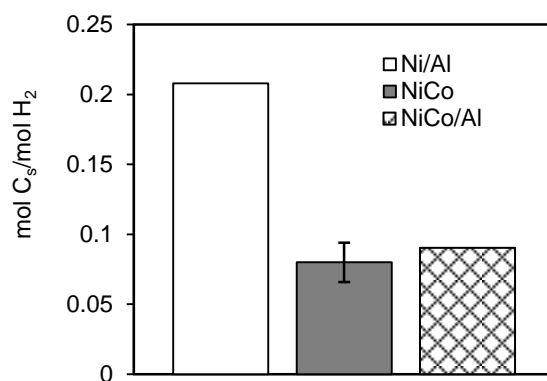


Figure C-1 Coke selectivity measurement from SR of acetic acid, 400°C, S/C=7.5, W=1.25g catalyst

The coke selectivity corresponding to the experiments performed at low conversions is presented on Figure C-. The conversion from these tests resulted in the range of 20-27% based on acetic acid disappearance. Single tests for each reaction show that coke selectivity decreased in the order: Ni/Al > NiCo > NiCo/Al. Co addition in this case may still inhibit coke formation while keeping hydrogen productivity when compared to especially the Ni/Al catalyst. A small difference between the supported and unsupported NiCo catalysts may suggest the important role the Al₂O₃ support plays in the SR reaction. From these results it could be speculated that the coking phenomenon may not depend only on the support but may also be influenced by a synergistic effect of the supported metals.

Carbon deposition for the high conversions tests represented mostly around 1% of the mass balance with the exception of Ni/Al which was closer to 2% of the mass balance. Again, it also must be considered that the coke generation needs to be compared to the reforming products to eliminate the effect of selectivity to other byproducts like CH₄, CO, acetone, and even the effect of the excess water. These last results were found to support the behavior observed during the experiments under kinetic control at the low SR as defined for the coking study for Chapter 4.

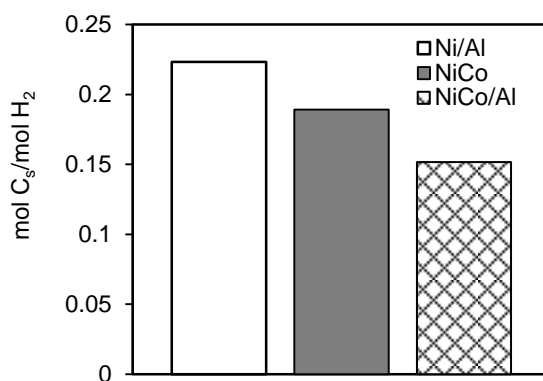


Figure C-2 Coke selectivity measurement from SR of acetic acid, 400°C, S/C=7.5, W=50mg catalyst

The characterization of the catalyst used for this independent study has been presented on Chapter 4. The SEM micrograph shown on Figure C-3 seems to show that metal clusters on the NiCo/Al were formed and dispersed over the Al₂O₃, which appears as a less dense material around this cluster shown. EDS (Electron Dispersive X-Ray Spectroscopy) analysis showed that both Ni and Co were enriched in this phase. Proving that intimate contact between existed between the two metals on the supported formulation. Strong peaks on the XRD analysis were shown for the formation of NiCo spinel that may be responsible for the results shown.

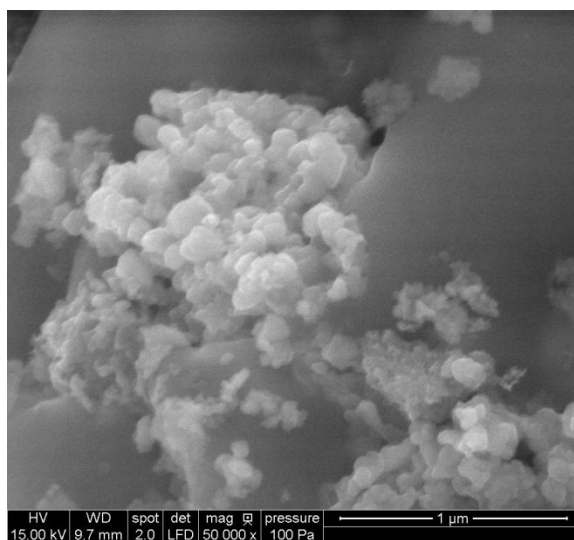


Figure C-3. SEM-SE image of the prepared NiCo/Al₂O₃ at 50,000x

On Figure C-, EDS analysis of a coked NiCo/Al catalysts particle. It can be observed that the Ni is almost not detected as it could be covered by carbon especially where the carbon is enriched. Conversely there are areas enriched in Co that are not covered by carbon. From the XRD analysis, very little elemental Co was found compared to the NiCO spinel. This result seems to vaguely suggest that coke over Co enriched areas is less likely to happen than over Ni enriched areas or even the catalyst support.

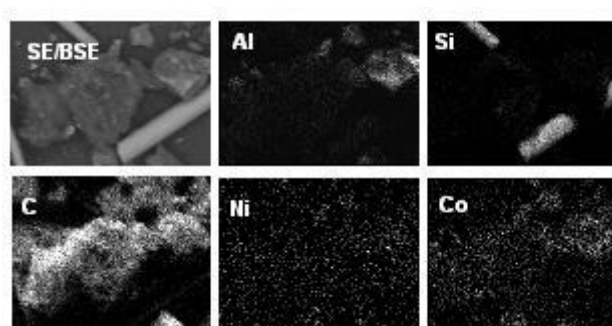


Figure C-4. SEM-EDS map of coked NiCo/Al₂O₃ at 300x

A SEM micrograph of a close-up of the coke formed over the NiCo/Al catalyst during SR of acetic acid was included as reference (Figure C-5). Both figures for coked catalyst correspond to coke formed during acetic acid SR at 460°C with S/C of 6.

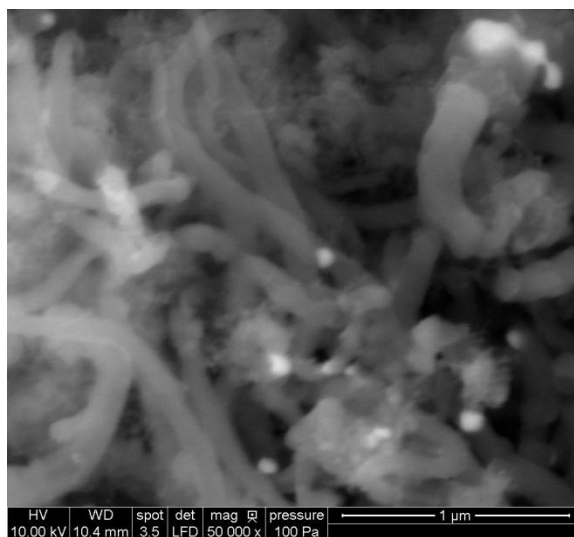


Figure C-5. SEM-SE image of coke deposited from SR of acetic acid, 460°C

The coke observed here seemed somehow translucent. This describes its relative density and perhaps supports the idea that the carbon formed under these conditions is not graphitic in nature, but rather amorphous and easier to activate and gasify.

Conclusions

The use of a bimetallic NiCo catalyst for acetic acid SR at low temperature has shown improvement over a baseline Ni/Al reforming catalyst at high conversions in terms of coke formation relative to hydrogen production. When reactions were performed with a limited conversion to show kinetic behavior it still seemed to improve over the Ni/Al and especially the supported NiCo/Al. This preliminary result may suggest that dispersing the bimetallic catalyst over an Al₂O₃ support may help reduce coke formation. This is of course in contrast to what has been discussed in the literature, where acetic acid allegedly tends to ketonize leading to oligomeric coke over acid supports like alumina.[2,3]

These reaction tests were performed to set the basis for enhancement by using a bimetallic NiCo catalyst to reduce coke formation from acetic acid SR. If coke formation can be hindered from this troublesome species this catalyst would become very relevant for improving the reaction characteristics of water-soluble bio-oils.

References

1. Hu X, Lu G: Investigation of steam reforming of acetic acid to hydrogen over Ni-Co metal catalyst. *Journal of Molecular Catalysis A: Chemical* 261(1), 43-48 (2007).
2. Takanabe K, Aika K-I, Inazu K, Baba T, Seshan K, Lefferts L: Steam reforming of acetic acid as a biomass derived oxygenate: Bifunctional pathway for hydrogen formation over Pt/ZrO₂ catalysts. *Journal of Catalysis* 243(2), 263-269 (2006).
3. Wang D, Montane D, Chornet E: Catalytic steam reforming of biomass-derived oxygenates: Acetic acid and hydroxyacetaldehyde. *Applied Catalysis a-General* 143(2), 245-270 (1996).

Appendix D. Combined Catalyst-Sorbent for Bio-oil Steam Reforming

This appendix is a partial representation of the following report:

Environmental Enhancement through Corn Stover Utilization
USDA Grant No. 68-3A75-5-233

Final Reprot Task 1 Bio-oil Production (ISU-CSET)

Principal Author: Robert C. Brown

Other Authors: Pedro J. Ortiz-Toral, Marjorie Rover

Note: This report does not contain patentable material, protected data, or information of a proprietary nature that may otherwise limit its disclosure and use.

Project Goals and Objectives

The overall Objective of Task 1 was to develop a pyrolysis process, which will produce bio-oil and char materials from conversion of cornstover in quantities and qualities that make them suitable for their end uses. Goals:

1. Determine operating conditions yielding appropriate fractions of bio-oil, char, and gas from cornstover.
2. Produce bio-oil for use in steam reforming trials.
3. Produce lignin-rich and carbohydrate-rich fractions of bio-oil.
4. Test catalyst/sorbent pellets for production of hydrogen from bio-oil.

Experimental Results and Discussion

The work includes the following:

1. Completion of the construction of a new 8kg/hr fast pyrolyzer system equipped with fractionating bio-oil collection system. This work is supported by a Department of Energy research grant.
 - System is fully operational.
2. Fractionated bio-oil and char samples have been produced.
 - Bio-oil successfully collected in fractions: lignin-rich, carbohydrate-rich and water-rich fractions
3. Bio-oil and model compounds have been reformed by using commercial catalyst and ISU's novel catalyst-sorbent catalyst.

- Hydrogen purity was obtained at 98% with the core-in-shell material

Emphasis of the work has been on bio-oil reforming study. Specific details of the work completed during years 3 and 4 are described below.

Production of Bio-oil Fractions by Using New Fast Pyrolysis System

In the past two reporting periods, bio-oil and char have been produced by fast pyrolysing biomass by using an existing 8kg/hr fast pyrolysis system at Iowa State University (ISU). As reported in the previous year's annual reports the fast pyrolysis experiments using cornstover as the feedstock showed limited success. Some of the problems with the existing system and incompatibilities with cornstover were resolved during the previous year's work; however, many of the problems continued to hinder the optimization and successful production of bio-oil and char from cornstover despite additional efforts to improve the unit. Schematic diagram of the fast pyrolysis system is shown in Figure 2. Details of the reactor system and issues related to its capability in producing bio-oil have been reported in the 2008 annual report.

A new research funding granted by the Department of Energy has enabled ISU to design and build a new much improved fast pyrolysis system. The system was designed based on the configuration of the former fast pyrolysis system. The small pilot unit consists of a fluidized bed reactor, which is heated externally by electrical heater, a staged auger-type biomass feeding system, a char removal system, and a bio-oil vapor collection system, which allows bio-oil to be collected into several fractions with different properties and chemical compositions. An Intellectual Property (IP) application has been submitted for the fractionating bio-oil collection system. The new fast pyrolysis system has been operated with a much improved success by using various types of biomass materials.

Several selected bio-oil samples obtained from several selected fast pyrolysis run were analyzed for their physical and chemical properties. The chemical and physical characterization measurements on the bio-oil samples were done by using the following methods:

- Chemical characterization
 - CHNS-O analyzer (C, H, O, N, S elements)
 - GC/MS (chemical composition)
- Physical characterization:
 - Ash content
 - Water insoluble content
 - Karl-Fischer titrator (water content)

Figure 1 and Table 1 below the GC/MS chromatograms and the properties of five bio-oil fractions from one fast pyrolysis test run using oak wood at 500°C. Figure 1 shows the chromatograms of fractions 3, 1, 2, 4, and 5 (from top to bottom). The chromatograms clearly show that the distribution of chemical compounds within each fraction is quite different. Fractions 1, 2, 3 and 4 show a significant presence of heavy components (phenols and sugars) while the presence of low MW components are more pronounced in fraction 5. Table 1 show that the presence of water is concentrated in fraction 5, which also has the highest total acid number.

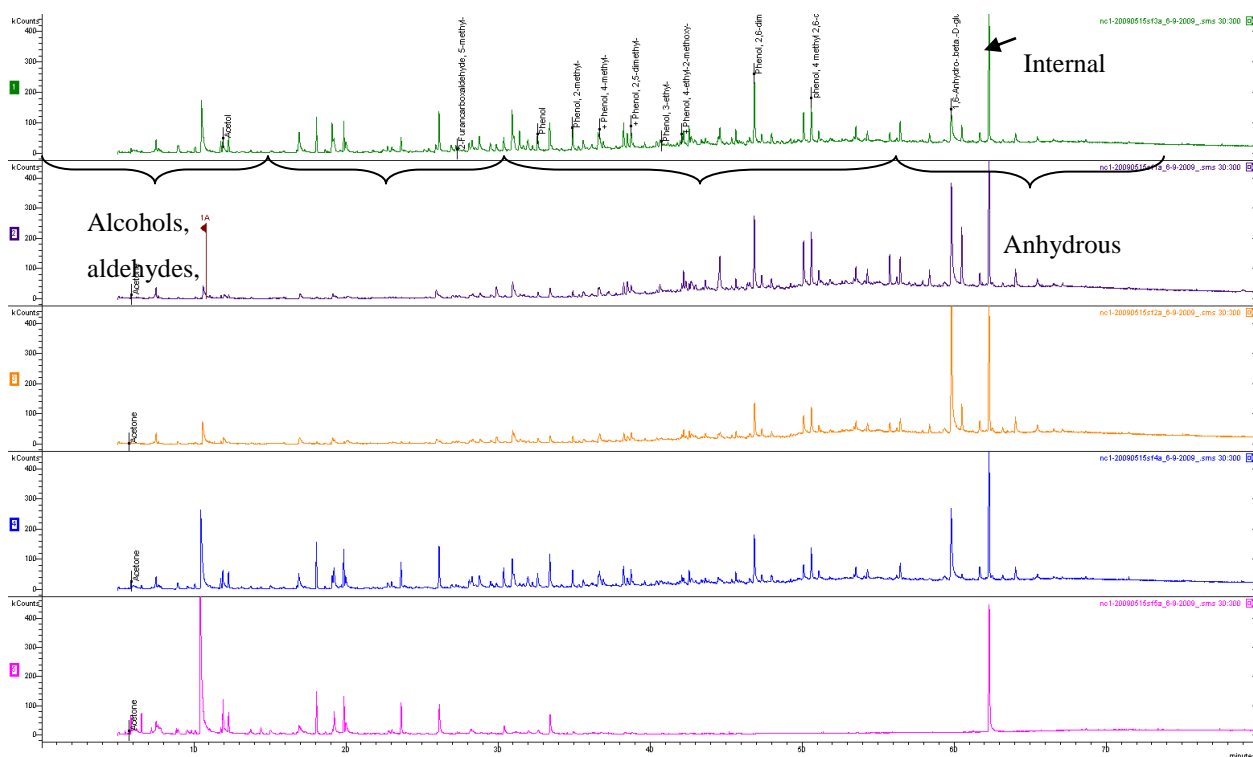


Figure D-1. GC/MS chromatograms of bio-oil fractions produced from fast pyrolysis of oak wood at 500°C produced by using the new ISU fast pyrolysis system.

Table D-2. Properties of bio-oil fractions collected from fast pyrolysis of oak wood using ISU fast pyrolysis system.

Analysis of Bio-oil Fractions Produced from Fast Pyrolysis of Oakwood									
Fraction #	Water Insolubles	Total Acid Number	Analysis by TGA		Moisture Content (by KF Titration)	Elemental Composition (w/ water)			
			Fixed Carbon	Ash		%C	%H	%N	%O*
1	49.15	36.9	32.16	0.84	2.58	59.1	6.1	0.34	34.5
2	40.93	42.3	29.08	0	6.62	58.6	6.4	0.15	34.8
3	20.03	57.7	20.44	0	4.67	52.2	6.7	0.14	41.0
4	28.85	84.6	22.64	0.41	7.76	50.6	6.6	0.10	42.7
5	0.32	133.6	2.74	0.23	53.38	19.2	9.0	0.01	71.8

Catalytic steam reforming of bio-oil

While the primary work on bio-oil reforming is conducted by NREL in Task 2, a study on bio-oil steam reforming has been conducted as part of Task 1. The context of this work was focused on the production of hydrogen from the water-soluble stream of bio-oil after the water insoluble fraction was separated as a higher-value product. A basic understanding of the complex SR (steam reforming) characteristics of these bio-oil products was sought to be able to recognize the causes of the issues like limited reaction times. It is important to understand the nature of the reactions to ultimately minimize the issues.

ISU has developed a novel combined catalyst/sorbent material that allows simultaneous steam reforming of organic compounds to hydrogen and separation of the produced carbon dioxide. The material, called core-in-shell catalyst-sorbent, consists of a highly reactive lime core enclosed within a porous protective shell made of alumina that is loaded with the reforming metal catalyst. The *in situ* removal of carbon dioxide could shift equilibrium towards increased hydrogen yields. Previous tests with methane and toluene showed hydrogen yields that were as high or superior to those achieved with conventional multi-step reaction and separation processes.¹

First, the steam reforming characteristics of fractionated bio-oil were studied by using a commercial reforming catalyst. From these tests the most suitable fraction for hydrogen production was identified. The performance of laboratory prepared core-in-shell reforming catalyst was tested for a very relevant oxygenated bio-oil model compound. Finally, a light-end bio-oil fraction of bio-oil was reformed with two different formulations of core-in-shell catalyst. One of these catalysts was a nickel based core-in-shell and the other was an iron oxide based core-in-shell formulation.

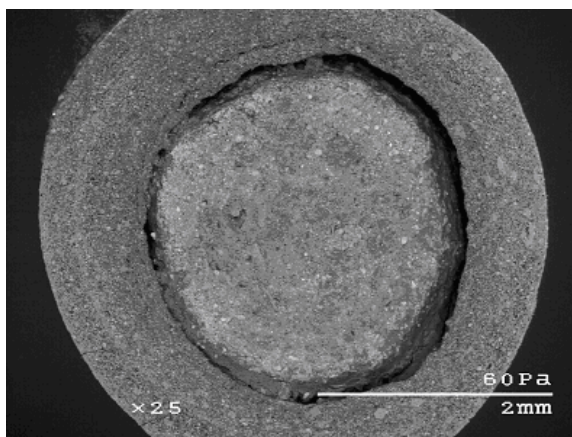


Figure D-2. SEM micrograph of a core-in-shell catalyst-sorbent pellet for steam reforming of hydrocarbons.

Core-in-shell catalyst synthesis

Microna 3 limestone powder was pelletized to spheres inside a rotating cone using deionized water. The target size for the spheres was between mesh #5 and #6. The cores were hardened by rotating at 10 rpm for 10 min., 30 RPM for 20 min., 60 RPM for 30 min., and 90 RPM for 30 min. This was done while avoiding adding too much water so that the pellets do not start to clump. Once the cores are hardened the shell was applied.

For the Ni/Alumina shell formulation, the shell material was made of a mixture of 10 wt% limestone powder, 27 wt% DD-290 amorphous alumina (Al_2O_3), 27 wt% T-64 alumina, and 36 wt % A16-SG alumina. The powder was slowly added to the cores in the rotating cone at 30 RPM spraying sparingly with DI water as binder. The pellets were kept at a size between

sieves #4 and #5. The material was then calcined at a temperature of 900°C over a period of 3 hrs under air flow. Upon cooling down, carbon dioxide was applied and heated to 650°C to obtain the carbonate (limestone). Nickel metal was applied via impregnation method with a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in THF. The pellets were drained, dried and calcined to 500°C for 2hr to decompose the salt to nickel oxide. Reduction of the catalyst was required to obtain the active elemental nickel.

For the case of the iron oxide (Fe_2O_3 /Alumina) core-in-shell formulation the iron was incorporated to the alumina precursor shell mixture. The shell mixture was made of 10 wt% Microna Limestone, 27 wt% DD-290 amorphous Al_2O_3 , 27 wt% T-64, 36 wt % A16-SG, and 10 wt% iron oxide. The mix of powders was applied to the cores and to later be calcined at 900°C for 3 hrs. Then the core material in the catalyst was re-carbonated to calcium carbonate.

Core-in-shell reactor tests of model compound

Reforming tests were performed in the fixed bed reactor setup described earlier at 500, 550 and 600°C at different S/C ratios ranging from 2 to 6. Reactions were performed with both the commercial catalyst and the core-in-shell catalyst for comparison. Sorption enhanced reactions were performed at 550°C following a protocol based on Satrio et al., showing a period of high hydrogen concentration up to 98% (when normalized to exclude nitrogen) followed by a transition period until saturation was reached. The figures show the gas product concentration relative to the nitrogen internal standard.

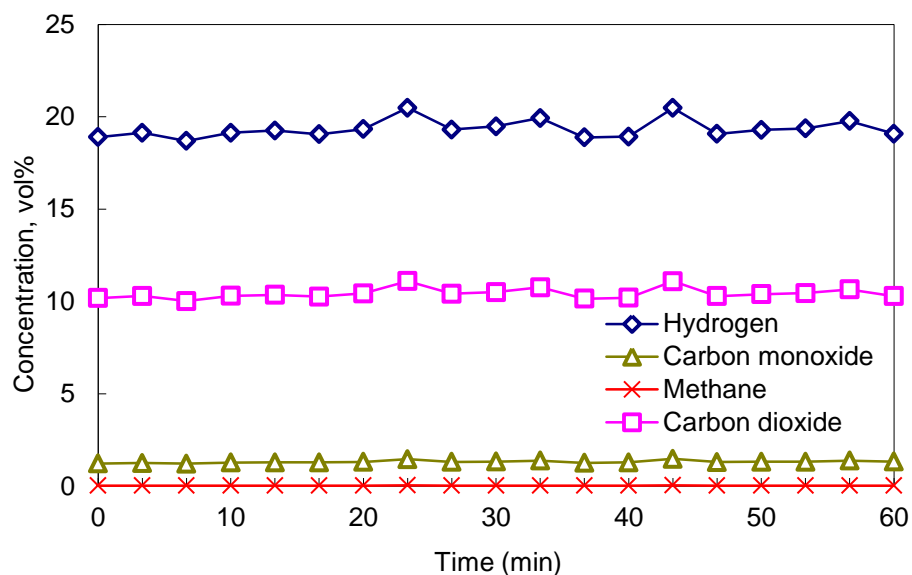


Figure D-3. Acetic acid SR with the commercial catalyst, S/C=6, 550°C

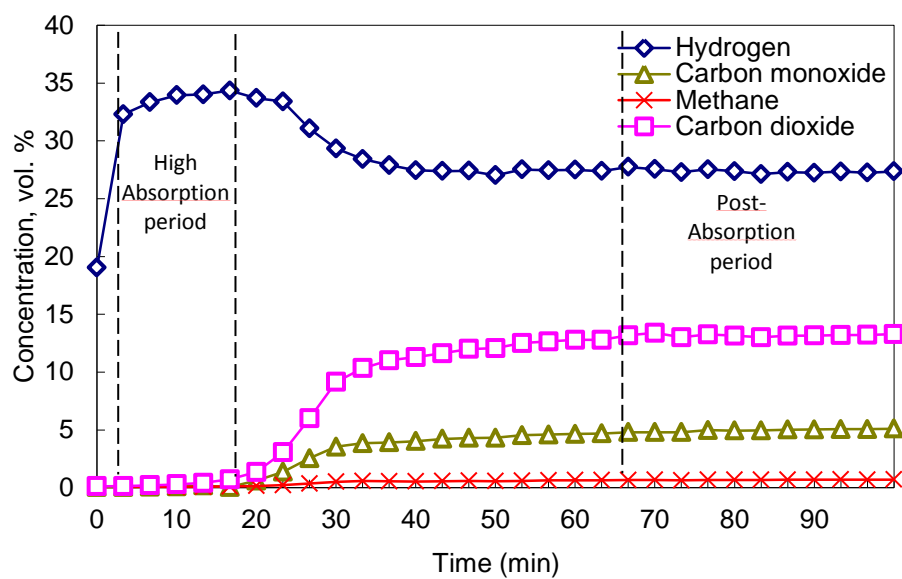
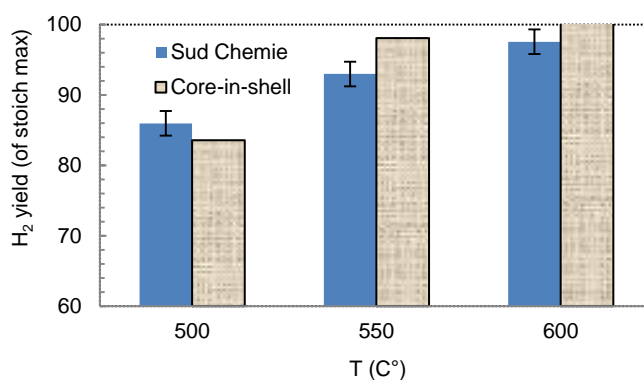


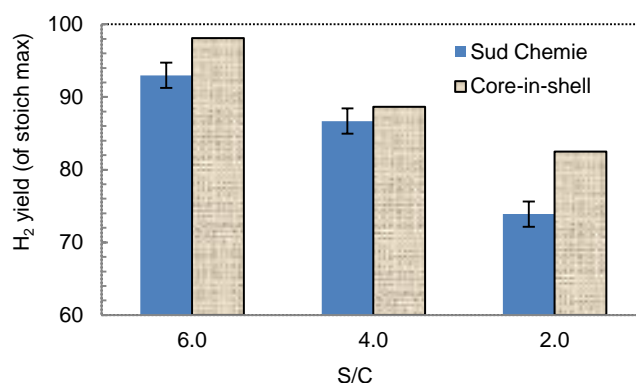
Figure D-4. Acetic acid SR with core-in-shell catalyst, S/C=6, 550°C

The core-in-shell catalyst was able to perform the reforming of the acetic acid to completion but the absorption activity decreased quickly. This is either due to the quick saturation of the core material due to insufficient available sorbent surface or due to a diffusion limitation

caused by the progressive carbon deposition on the shell. This will be further studied to understand better the reasons for these short times and to ultimately make recommendations for core-in-shell formulation. The data presented in figures 6 and 7 represents the hydrogen yield at steady conditions for the Reformax 330 catalyst and during the absorption period for the core-in-shell. It was observed that the hydrogen yield was maximized at temperatures in the vicinity of 550 and 600°C.



FigureD-5. Temperature effect on SR of modeled bio-oil



FigureD-6. Test for enhancement at low water levels (demanding conditions)

It is apparent that the core-in-shell material performed slightly better at these temperatures. Then the reaction was tested at three different S/C molar ratios to study possible enhancement at lower water addition levels. It was hypothesized that the thermodynamic effect of the CO₂ removal would improve the hydrogen production under demanding

conditions. It can be observed that the core-in-shell performed better at the lower water addition levels, giving hydrogen yields above 80%.

Core-in-shell reactor tests of light bio-oil fraction

A light-end bio-oil fraction was obtained from a fast pyrolysis unit at Iowa State University. This pyrolysis unit is different from the employed in the earlier work. The new proprietary condenser system has been built to provide a better separation of the bio-oil fractions. In this case the bio-oil used was obtained from red oak biomass. In this case the fraction called SF6 was analyzed to contain 55.5% water by KF titration and composed mostly of acetic acid. Elemental analysis of CHN was also performed (C: 17.93%, H: 8.80, O: 73.27) to determine the intrinsic S/C molar ratio in the fraction to be 2.06.

Table D-2. GC and Karl Fisher characterization of SF6 bio-oil

	wt%
Acetic acid	14.09
Furfural	1.02
Glycolaldehyde	2.29
Acetol	5.55
Methanol	1.41
Acetone	0.78
Water	55.5
Mass Balance	80.6

The bio-oil for this case was filtered and fed to the reactor without any water addition. 1.25g of the Reformax 330 catalyst was used while the liquid feeding was 6.0mL/hr, and this represents about $1700 \text{ hr}^{-1} \text{ G}_{\text{C1}}\text{HSV}$ (gas hourly space velocity if all carbon was considered as methane). The resulting gas profiles are presented in the following figure.

After following the protocol described before the stoichiometric hydrogen yield was estimated to be 71.6%. This value is similar to the value previously seen for the cond. 4 bio-oil that had a S/C of about 8. This fraction showed initially that it does not need addition of water to supplement the reforming reaction in order to obtain high hydrogen yields. A considerable amount of carbon deposits was observed, nevertheless, after the reaction.

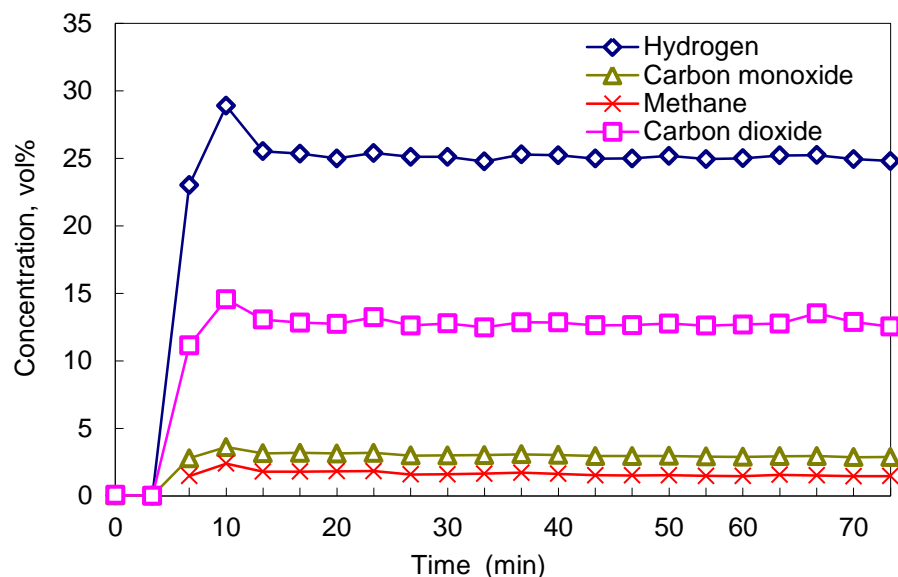


Figure D-7. SR profile of SF6 bio-oil with commercial catalyst, T=550°C, S/C=2.06

A temperature-programmed oxidation or TPO analysis was performed and the carbon profile was generated showing different kinds of deposits. Some of these deposits were reactive and easily removed while the most prominent appeared at the higher temperatures. A significant amount of the carbon was found at temperatures similar to the case of acetic acid for example. The peak of highest amount of carbon detected was at around 650°C which shows a more stable and possible amorphous form of carbon deposited.⁷ The quantification analysis from this test showed a molar carbon deposit yield of 29.8%.

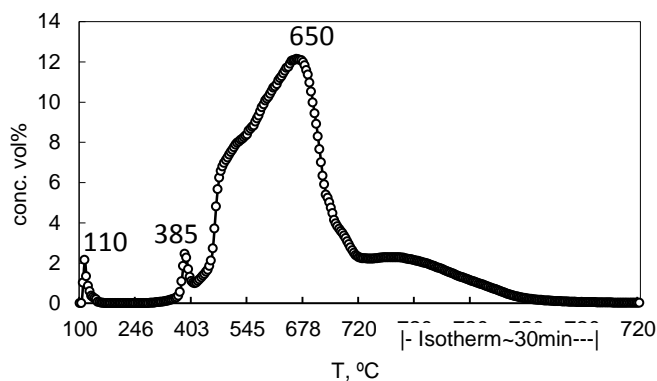


Figure D-8. TPO profile of deposits after SR of 1-20090608A-SF6 bio-oil

SR of the light end bio-oil was then performed over the Ni/Alumina/CaO core-in-shell material. Hydrogen production was detected within the first 5 min after starting feeding, together with small amounts of CO₂ and CH₄. For the whole bio-oil hydrogen was produced at 98% purity for a period between 8-12 min. The high CO₂ absorption period was used for yield calculations. This period was followed by a transition from the highly pure hydrogen into a mixture of hydrogen, carbon dioxide, and methane (26-32 min). A steady concentration of the product gases was eventually observed and identified as the post-absorption period. It was found that during this period the products closely match the products from the reactions performed over the commercial Ni/Alumina catalyst.

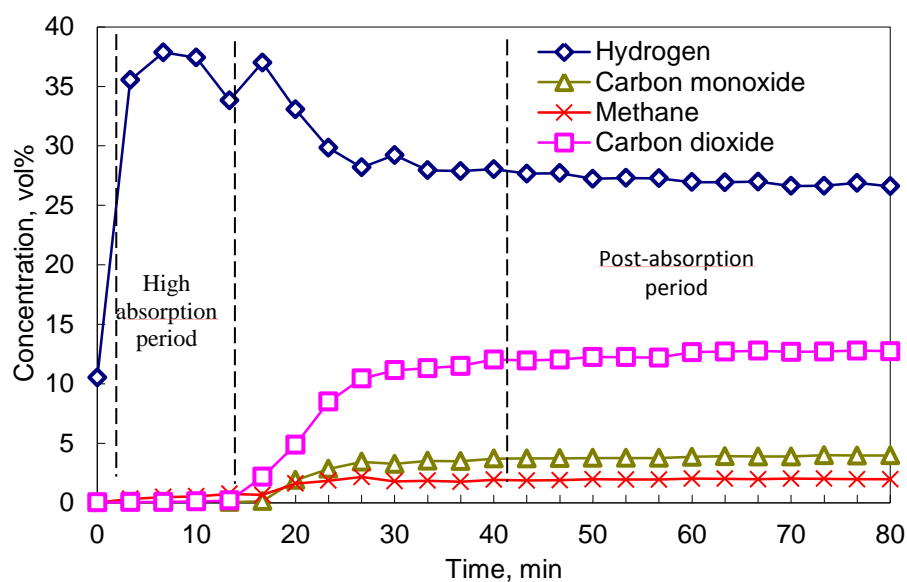


Figure D-9. SR of SF₆ bio-oil with Ni core-in-shell catalyst, , T=550°C, S/C=2.06

For the case where the bio-oil was adjusted to a S/C ratio of 6, a longer high-absorption period was observed (about 35 min). This could be a consequence of lower input of bio-oil species as the solution was more diluted but could as well be a result of decreased limitation by carbon deposition. One of the reasons for the low absorption periods could be based on the fact that carbon dioxide is readily produced at the selected reaction temperature. This could have caused the lime sorbent to saturate very quickly.

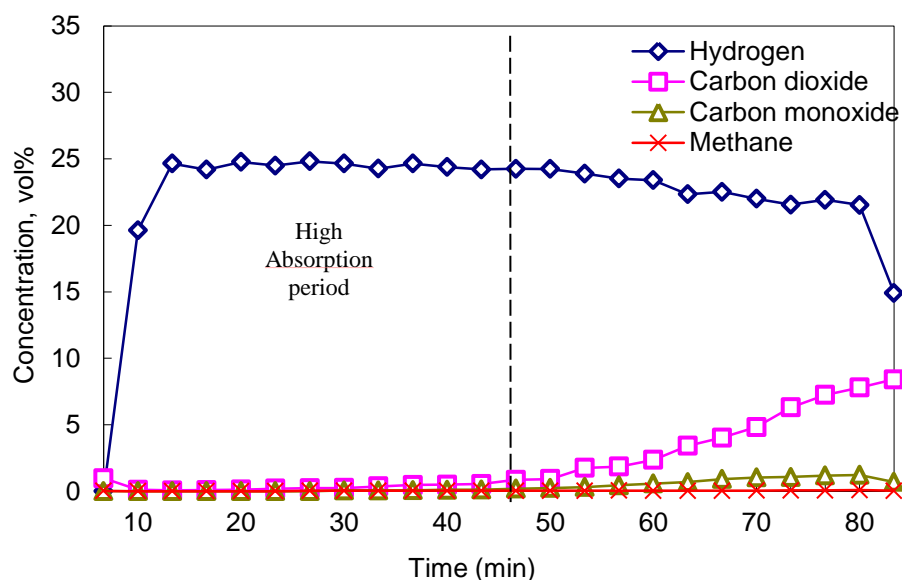


Figure D-10. SR of light fraction of bio-oil Ni core-in-shell catalyst, $T=550^{\circ}\text{C}$, $S/C=6$

This same effect could have been produced as a consequence from the observed rapid carbon deposition. Carbon deposits could have fouled the pore structures of the shell, thus limiting the diffusion of the carbon dioxide into the sorbent core. Although many methods exist to study the extent of carbon deposition (gravimetric, temperature program oxidation, carbon balance, etc), given the nature of the material this resulted in a non-trivial question. During temperature program methods as the temperature increases, the carbon deposits start to convert mostly to carbon dioxide. At the same time the sorbent core starts to desorb decomposing the calcium carbonate into lime (CaO) skewing the results. In turn if the core is to be desorbed under inert atmosphere first, the carbon dioxide released could start to oxidize the carbon deposits at the elevated temperatures required.

A calculation was used to roughly estimate the sorption capacity of the core material. An assumption was made that about 10% of the weight of the core material is actually exposed and active for carbon dioxide absorption. After the first 19 minutes of hydrogen production the core material should be completely saturated. This rough calculation supports the idea that the cores were indeed quickly saturated.

Looking at the hydrogen yields in table D-3, the Ni core-in-shell catalyst shows enhancement during the high-absorption period compared to the performance of the commercial catalyst. This was observed for both the S/C ratios tested. Experimental error on the effluent volumetric measurements accounts for the above 100% stoichiometric yields in the case of the Ni core-in-shell catalyst. The effluent flow rate fluctuated especially towards the beginning of the reaction affecting more severely the measurements for core-in-shell catalyst during the high-absorption periods.

Table D-3. Hydrogen yields from SR reactions of SF6 bio-oil at 550°C

Metal phase	<i>Ni</i>				<i>Fe₂O₃</i>	
	Reformax		Core/shell		Core/shell	
Catalyst type	2.1	6	2.1	6	2.1	6
S/C molar ratio	2.1	6	2.1	6	2.1	6
H ₂ yield % (wt H ₂ /wt bio-oil) ^a	9.04	10.5	14.1*	12.7	2.3*	2.8
H ₂ stoich yield (mol%)	71.6	96	112*	116	17.9*	25.2

^a calculated on a dry basis, * average results from replicates

An alternative formulation of the core-in-shell catalyst was prepared based on an iron oxide (Fe₂O₃) and alumina shell over the limestone core. Iron oxide catalysts are known as high temperature shift catalysts. This different catalyst formulation can be used to attempt to explain the relationship between the catalytic and sorbent properties of the material in contrast with the results of highly active Ni formulation.

The iron oxide acted as a weaker reforming catalyst, producing lower hydrogen yields as seen in table D-3. The lower activity allowed for a longer absorption period than that observed for the nickel based catalyst. This catalyst also showed methane to be the most prevalent gas product. The presence of hydrogen coupled with very low amounts of carbon oxides may suggest that the rate of methanation was fairly high consuming carbon monoxide and hydrogen.

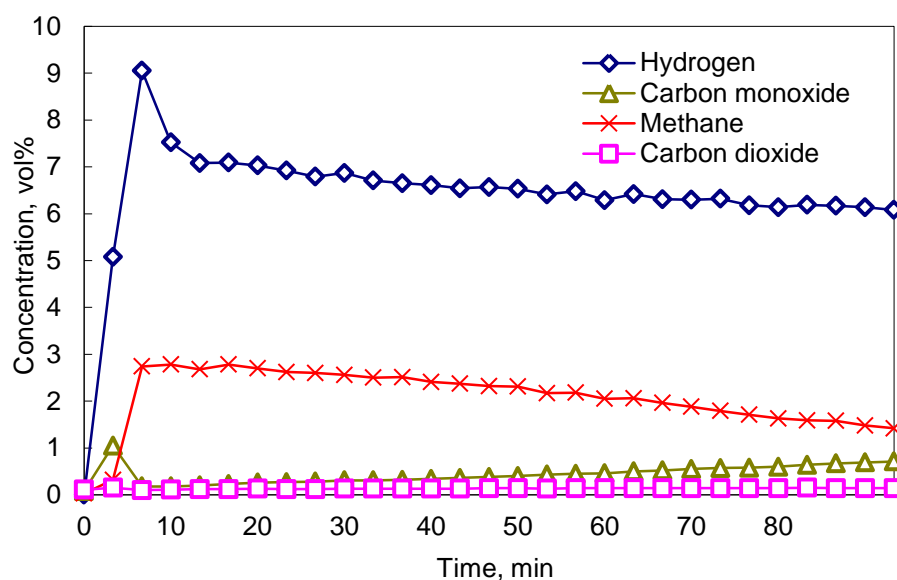


Figure D-11. SR of light fraction of bio-oil over Fe_2O_3 core-in-shell catalyst, $T=550^\circ\text{C}$, $S/C=6$

Otherwise come of the hydrogen could have been produced via a Boudart reaction. The latter reactions makes sense is we consider the deactivation pattern consistently observed for the reactions with the iron oxide catalyst formulation. The longer absorption period also supports the idea that the carbon deposition does not necessarily limit the diffusion of the carbon dioxide to the sorbent core.

Conclusions

A different extent of carbon deposition affect the SR product yields depending on the fraction or type of bio-oil reformed. The presence of low molecular weight acetic acid and acetol seem to promote higher hydrogen production. While the presence heavier molecules like levoglucosan and furfural may have a detrimental effect in the hydrogen production. An overall relation was detected between the molecular weight of the molecules reformed to the ability to reform and possible extent of carbon deposition. These effects observed cannot be completely deconvoluted by studying complex mixtures. Aqueous bio-oil is unstable and some of its properties change upon storage, generating difficult to characterize suspended oligomers. The aging of the aqueous bio-oil samples proved to be detrimental for hydrogen production via SR.

On the other hand, the development of new fractionation systems could show opportunities for better separation of species in different fractions so that they could be used for different applications depending on their properties. For example, an oligomer-free, lighter fraction, with low mineral content, and higher moisture content could be ideal for hydrogen production while heavier ones could be upgraded via processes like hydrodeoxygenation employing the hydrogen generated.

It can be clearly observed that at temperatures as low as 550°C the SR and WGS reactions occur essentially to completion. With the use of a core-in-shell catalyst which included the sorbent core, the carbon dioxide is absorbed and thus removed from the product stream for certain amount of time. During this time the production of carbon monoxide and methane were also limited showing improved WGS and limited methanation reactions for the case of nickel based formulation. In the case of iron based core-in-shell the methanation reaction seemed to be too fast compared to the SR therefore methane was a major product.

Overall the use of the core-in-shell catalyst represents a shift in the equilibrium reactions that could result in an increase in hydrogen yield together with the ability to produce high concentration of hydrogen. This shift may not seem as drastic as the shift observed in sorbent enhanced methane SR. There are a series of remaining challenges like improving the strength of the core-in-shell materials and improving the sorption capacity to minimize the need for repeated regeneration steps.

References

1. Satrio, J. A.; Shanks, B. H.; Wheelock, T. D., A combined catalyst and sorbent for enhancing hydrogen production from coal or biomass. *Energy & Fuels* **2007**, 21, (1), 322-326.
2. Daugaard, D. E.; Brown, R. C., Enthalpy for Pyrolysis for Several Types of Biomass. *Energy Fuels* **2003**, 17, (4), 934-939.
3. Daugaard, D. E. The transport phase of pyrolytic oil exiting a fast fluidized bed reactor. Iowa State University, Ames, 2003.

4. Kechagiopoulos P.N.; Voutetakis S.; Lemonidou A.; I, a. V., Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-oil in a Fixed Bed Reactor. *Energy and Fuels* **2006**, (20), 2155-2163.
5. Mohan, D.; Pittman, C. U.; Steele, P. H., Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels* **2006**, 20, (3), 848-889.
6. Trimm, D. L., Coke formation and minimisation during steam reforming reactions. *Catalysis Today* **1997**, 37, (3), 233-238.
7. Tian, L.; Zhao, X. H.; Liu, B. S.; Zhang, W. D., Preparation of an Industrial Ni-Based Catalyst and Investigation on CH₄/CO₂ Reforming to Syngas. *Energy & Fuels* **2009**, 23, (2), 607-612.